July, 1928

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VOLUME I NUMBER 2

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Editor.....C. C. Davis
Associate Editor.....H. L. Fisher
Secretary-Treasurer.....H. E. Simmons

Vol. I July, 1928 No. 2

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RUBBER CHEMISTY AND TECHNOLOGY

Rubber Chemistry and Technology is published periodically under the supervision of the editors representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important published papers on fundamental research, technical developments and chemical engineering problems relating to rubber or its allied substances.

Members of the American Chemical Society who are also paid members of the Rubber Division are entitled to receive this publication. Any other individual corporation or organization interested in rubber, though not a member of the American Chemical Society, is eligible to become an associate member of the Rubber Division upon payment of $6.00 annually and is thereby entitled to receive this publication.

All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address and missing numbers and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, Professor H. E. Simmons, Easton, Pa., or Municipal University, Akron, Ohio.

Rubber Division Activities

H. E. Simmons, Secretary-Treasurer of the Rubber Division of the American Chemical Society

The Rubber Division of the American Chemical Society

Officers

Chairman.....Harry L. Fisher, United States Rubber Co.
Vice Chairman.....Arnold H. Smith, Rubber Service Laboratories
Secretary-Treasurer.....H. E. Simmons, Municipal University of Akron
Executive Committee..H. A. Winkelmann, E. R. Bridgwater, Stanley Krall, J. M. Frye, W. G. Nelson.

Minutes of Recent Meetings

St. Louis Meeting

Minutes of the St. Louis Meeting of the American Chemical Society, Coronado Hotel, Wednesday, April 18, 1928.

The meeting was called to order by the Chairman, Dr. Harry L. Fisher, at 9:40 with 150 members present. The program arranged was carried out complete. At the close of the presentation of papers, Mr. Krall read a report of the Committee on Physical Testing as prepared by the Chairman, Mr. Partenheimer, as follows:

Progress Report of Committee on Physical Testing

The Progress Report read at the Detroit meeting last September has been revised and published in the December 10th issue of *The Rubber Age*. In this Report the Committee recommended that "mixed stock prior to curing be conditioned not less than 24 hours nor more than 28 hours at an absolute humidity of 5.24 grains of water per cubic foot of dry air and cured stock prior to testing be conditioned for not less than 24 hours at 82° F. ± 2° and 45% relative humidity ±3%." This recommendation was criticized on the grounds that we did not have sufficient evidence to prove that mixed stock conditioned at the same absolute humidity and at widely different temperatures would give the same test results. Subsequent work was therefore carried out which showed the recommendation to be sound. The uncured stocks were exposed to an absolute humidity of 5.24 grains of water per cubic foot of air at temperatures of 70° F. (21.1° C.), 82° F. (27.9° C.), and 90° F. (35° C.). The range of temperatures covered—70° F. to 85° F.—will, we believe, include all temperatures which different laboratories will adopt for conditioning uncured specimens. Moisture absorption curves show that there is a slight increase in rate of absorption at the lower temperatures, due to the increased relative humidity, but the stress-strain data show that this increase in rate of absorption is not sufficient during a twenty-four hour period to affect the physical properties of the compounds to an appreciable extent.

A study has been made of the effect of variations in relative humidity before mixing, using the same five formulas used in the previous investigation. The rubber and compounding ingredients were exposed to relative humidities of 0, 35, 65 and 100% at 82° F. for six days prior to mixing. The compounds were made up on the basis of dry weight materials so that when the batches went to the mills the weights varied from 772.5 grams to 794.1 grams, a difference of approximately

22.0 grams for the same stock. After mixing, the same batches were all within one gram of the same weight indicating that nearly all the moisture was driven off during milling. The mixed stocks were all exposed to standard conditions both before and after curing. Negligible differences in tensile and stress-strain properties were obtained, so the Committee is not recommending any specific humidity conditions for storing rubber and compounding ingredients prior to mixing. It will be sufficient to exercise ordinary care in storing rubber and ingredients.

With the completion of the investigation of the effect of humidity before mixing, the Committee has finished the first problem undertaken—that of determining the importance of controlling humidity and temperature during the different stages of preparation and testing rubber test specimens for tensile and stress-strain properties. The detailed report of this investigation has just been released by the Bureau of Standards, but is not yet at hand. Arrangements will probably be made with the Rubber Association for distributing this report to members of the Association and the Society. There may be a small charge connected with the publication of this report, but we hope it will not be prohibitive.

The Committee has already started work on the next problem of determining the importance of controlling humidity and temperature during the different stages of preparation of the abrasion test samples and during the abrasion test itself. For this work the Committee has chosen Formulas (1), (4) and (5) which have been included in all the work thus far and a representative heel compound has been added.

Formulas	(1)	(4)	(5)	(Heel)
Smoked sheet	100	100	100	16.25–100
ZnO	5	5	5	2.00– 12.31
Sulfur	3	3.5	3.5	1.40– 8.62
Carbon black	...	40	40	7.00– 43.08
Di-*o*-tolylguanidine	0.75	1.25	...	0.25– 1.54
Captax	...	1	1.0	.....
Stearic acid	...	...	3.0	.....
Mineral rubber	...	5.0	...	.....
Pine tar	...	2.0	2.0	.....
Whole tire reclaim	...	...	...	45.20–278.16
Barytes	...	...	...	20.00–123.08
Dixie clay	...	...	...	7.40– 45.54
Paraffin	...	...	...	0.50– 3.08
				100

The Henry L. Scott Company and Grasselli Chemical Company have loaned the Committee the use of the U. S. and Grasselli Abrasion Machines. Preliminary work has been completed, showing that duplicate results can be obtained and we are now ready to start the first part of this investigation.

The finances of the Committee, amounting to $6000.00 for 1928, are now being handled by the Rubber Association. The amount includes the appropriation of the Firestone Tire and Rubber Company. When the Rubber Association took over the financing, the Committee had on hand $240.03, which was added to the Rubber Association fund. Mr. Scott made the Committee an attractive price on the Scott Testing Machine which had been loaned to the Committee since we started work, and the Committee now has the physical assets of one Scott Testing Machine.

Dr. Spear, Chairman of the Raw Rubber Specifications Committee, then submitted the following report:

Report of Raw Rubber Specifications Committee

A meeting of the Committee was held in Akron on February 28, 1928. A program was laid out as follows:

It was decided that the function of the Committee was to determine whether or not it is possible to formulate scientific testing procedures that may be useful in the purchase and sale of raw rubber.

The previous Committee, in its report of Sept. 10, 1926, page 4, second paragraph, propounded "Three fundamental difficulties. These are: First, lack of standard procedures; second, lack of check between laboratories on the same procedure; and third, difficulty of interpretation of results."

The present Committee decided to adopt a temporary procedure in order to determine whether or not the various laboratories represented on the Committee could obtain reasonably comparable results with the same rubber. The work has not yet proceeded to the point where the results may be submitted.

Reports from the Secretaries of the various groups were then given verbally.

Resolutions Committee

The Resolutions Committee, consisting of Messrs. Brier, Zimmerli, Hamblett, then submitted a resolution as follows:

The Rubber Division of the American Chemical Society wishes to express its deep appreciation to the Rubber Association of America for its generous support, without which it would not have been possible to publish in its present form the new journal of the Division, RUBBER CHEMISTRY AND TECHNOLOGY. The Rubber Division wishes also to express the same appreciation for the support of the Association in making possible a continuation of the work of the Rubber Testing Committee of the Rubber Division.

It was moved that this resolution be adopted and that the Secretary be instructed to forward copies of this resolution to the Secretary of the Rubber Association of America and likewise to each member of the Board of Directors. The Rubber Division moved that a copy of the same resolution be sent to H. S. Firestone.

The Resolution Committee then submitted Resolution No. 2, which was adopted unanimously and is as follows:

The Rubber Division of the American Chemical Society congratulates Mr. C. C. Davis, Editor, and his associates for the splendid achievement represented by the first issue of RUBBER CHEMISTRY AND TECHNOLOGY and extends its hearty thanks for the extensive service generously rendered in the preparation of this publication.

By Resolution No. 3, the Secretary of the Division was instructed to express the appreciation of the Division for the cordial welcome and reception by the St. Louis Section.

It was moved that a Chairman appoint a Committee of three to work in connection with Dr. Parsons in order to raise sufficient funds to take care of *Chemical Abstracts* for the next five years.

At a meeting of the Executive Committee held Wednesday noon, it was decided that for those members of the Division who desired additional copies of RUBBER CHEMISTRY AND TECHNOLOGY, a charge of $2.00 would be made for each additional copy, or a subscription price of $6.00 per year.

H. E. SIMMONS, *Secretary-Treasurer*

Akron Group Meeting

The second meeting of the Akron Group was held April 25, 1928, in the general office dining-room of the Goodyear Tire and Rubber Co. with an attendance of approximately four hundred seventy-five rubber technologists.

The program prepared under the direction of H. A. Winkelmann, Chairman of the Group, and W. H. Fleming, Chairman of the Program Committee, covered the general subject—"Factors Affecting Mill Room Operations." The principal paper of the evening was by N. W. Pickering, Manager of the Roll Dept. of the Farrell-Birmingham Co., on the subject, "Chilled Iron Rolls in the Rubber Industry."

Other papers included: "Power Variables in Milling and Mixing Rubber," by P. S. Shoaff; "Breakage of Mill Rolls," by J. E. Noonan; "Experiences with Mill Roll Speeds, Gear Ratios and Batch Sizes," by E. C. Zimmerman, and "Open Mill Mixing versus Internal Mixers," by P. P. Crisp.

The committee in charge of arrangements for the dinner included G. K. Hinshaw, J. M. Frye, W. H. Fleming, and Harold Gray.

To date, the Akron Rubber Group shows an accession of membership of forty-eight new members of the Rubber Division and of one hundred thirty-four associate members.

New York Group Meeting

The second meeting of the New York Group of the Rubber Division was held at the Town Hall Club, New York City, on April 26, 1928. It was preceded by a dinner at which one hundred thirty-four were present, the attendance at the meeting being approximately one hundred fifty.

At the close of the business session, a paper on "Recent Scientific Advances in Connection with Guayule," by Dr. David Spence, vice president of the Intercontinental Rubber Company, was read by Dr. Harry L. Fisher, Chairman of the Rubber Division, as Dr. Spence was unable to be present. Following this paper, motion pictures on the same subject were shown by Mr. George H. Carnahan, president of the International Rubber Company, the first two reels depicting the gathering of the shrub and extraction of rubber, in Mexico, and the remaining two showing the progress of guayule cultivation in California.

Of those present, one hundred seven enrolled as members of the New York Group.

Boston Group Meeting

The first meeting of the Boston Group was held in the main dining-hall of the Boston Chamber of Commerce, Boston, May 9, 1928.

The meeting was a great success, two hundred eighty-five persons attending the dinner and the addresses which followed. The meeting was under the direction of C. R. Boggs, Chairman of the local group of the Rubber Division, who presided at the dinner and at the presentation of the four papers.

Following the dinner, Mr. Boggs offered his greetings to the technical and non-technical guests in attendance, briefly outlined the history of the Rubber Division of the American Chemical Society, described the reasons which led to the formation of local groups, announced the establishment of the new Rubber Division journal, RUBBER CHEMISTRY AND TECHNOLOGY, urged all those interested in technical developments to become members or associate members of the Rubber Division with its privilege of receiving the new publication, and finally emphasized the opportunity for social and cultural enjoyment to be derived from frequent group meetings.

Mr. Everett Morss, President of the Simplex Wire and Cable Company, then described the early development of laboratories and technical departments in the rubber industry, and laid stress on the fact that no company can remain in the forefront of its industry unless it enthusiastically supports research and technical developments in its own organization.

Dr. H. L. Fisher, General Chairman of the Rubber Division of the American Chemical Society, was unable to be present, and a letter was read in which he expressed his regret and his best wishes for a successful meeting.

The meeting then continued with the presentation of four papers by prominent chemists and technologists. These were: "The Theory of Reinforcing Pigments," by J. T. Blake, Research Chemist of the Simplex Wire and Cable Company; "The Importance of Softeners and Dispersing Agents in the Manufacture of Rubber Goods," by J. M. Bierer, Technical Superintendent of the Boston Woven Hose and Rubber Company; "The Rate of Heat Transfer in Rubber Goods during Vulcanization," by T. K. Sherwood, Consulting Engineer of the Hood Rubber Company; "The Structure of Rubber and Its Importance in the Manufacture of Rubber Goods," by P. K. Frolich, Professor of Chemical Engineering at the Massachusetts Institute of Technology.

The four papers offered a wide range of subjects of technical interest, and were presented in such a manner that they were readily understood and appreciated by technical and by non-technical members alike.

The meeting closed with a feeling in the minds of all that the evening had been one of profit and enjoyment. Those in attendance included executives, salesmen, chemists, engineers, foremen and many others, forming a complete cross-section of the industry, and the satisfaction shown by such a gathering is proof of the interest, benefit, and educational value of local group meetings.

Los Angeles Group Meeting

The second meeting of the Los Angeles Group of the Rubber Division was held May 11, 1928, at the Mary Louise, Los Angeles, California, with R. B. Stringfield acting as temporary Chairman and Emmet S. Long as temporary Secretary. Fifty-two attended, compared with forty-three at the previous meeting.

After dinner, Mr. Stringfield presided at a short business meeting. Minutes of the former meeting were read and approved.

Mr. Park, Chairman of the Committee appointed at the previous meeting to prepare by-laws for this group, read the proposed by-laws, which were adopted unanimously.

Mr. Park suggested that the present temporary officers and Mr. Pond be re-elected and the following resolution was carried to the effect that the Secretary be instructed to cast a unanimous ballot for R. B. Stringfield, A. F. Pond, and Emmet S. Long, as President, Vice President, and Secretary-Treasurer, respectively, of the Los Angeles Group of the Rubber Division of the American Chemical Society to hold office until the next annual election of officers.

After a few minutes' intermission, Chairman Stringfield introduced the speaker, Dr. R. C. Riebl of Buitenzorg, Java, who is on the staff of the Research Institute for Rubber in North East Indies.

An interesting paper was then presented by Dr. R. C. Riebl of Buitenzorg, Java, of the Research Institute for Rubber in the North East Indies, dealing with the three phases of the Institute regarding the production of crude rubber.

J. P. McIntire, Chief of Production of the Calender Department of the Goodyear Tire and Rubber Company, then outlined the subject of Calendering, after which L. A. Whitcomb, Chief Engineer of the Goodyear Tire and Rubber Company, gave a comprehensive and instructive paper on the mechanical features of calenders, describing calender parts and numerous problems encountered in the process of rubber manufacturing.

Of great interest to all was the discussion next presented by our new friend, Dr. Kelly, Chief Chemist of Goodrich, on the weftless method of calendering, his talk being illustrated on the blackboard.

Mr. McIntire then closed the meeting after an interesting description of the profile thread calender and its method of operation.

EMMET S. LONG, *Secretary*

Financial Statement

Amount on hand February 22, 1928		$427.49	
Amount received in payment of dues Feb. 22 to June 6, 1928		985.00	
			$1412.49
Expenditures from Feb. 22 to June 21, 1928	$211.53		211.53
Balance on hand June 21, 1928			$1200.96

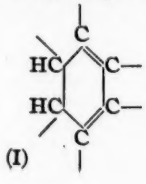
H. E. SIMMONS, *Secretary-Treasurer*

A Survey of Recent Literature on the Chemistry of Rubber

Abstracts of Articles Pertaining to the Chemistry of Rubber Which Have Appeared in Foreign and American Journals

The following abstracts are reprinted from the April 10 and 20, May 10 and 20, and June 10 and 20, 1928, issues of *Chemical Abstracts* and, with earlier and succeeding issues, they form a complete record of all chemical work published in the various academic, engineering, industrial and trade journals throughout the world.

$\Delta^{1,3}$-Dihydrobenzene, its derivatives and its polymerization products. FRITZ HOFMANN AND PAUL DAMM. *Mitt. schlesischen Kohlenforsch. Kaiser-Wilhelm Ges.* **2**, 97–146(1925); *Chem. Zentr.* **1926**, I, 2342–4.—Dihydrobenzene hydrocarbons of the general type (I) are of great interest, since they may be regarded as α,δ-disubstituted butadienes, and all butadienes are capable of forming terpenes and rubbers. This idea has already been substantiated for the simplest member of this class, *viz.*, $\Delta^{1,3}$-dihydrobenzene (II). For the prepn. of large quantities of II in pure form, none of the known methods is suitable. A better starting point is *1-amino-Δ^2-tetrahydrobenzene* (III), from the phosphate of which NH_3 is readily split off. The most advantageous method is to treat the easily obtained 1,2-dibromocyclohexane with NaOEt soln., whereby 20–30% (15–20% in large-scale prepns.) of II and 50–60% of *1-ethoxy-Δ^2-tetrahydrobenzene* (IV) are formed. IV is readily converted to II by $KHSO_4$. Of the derivs. of II, the SO_2 addn. compd. is of special interest, since it corresponds to the SO_2 derivs. of butadiene. II cannot, however, be recovered from this in quant. yield. The tendency of II to polymerize is considerably less than that of the open butadienes, and a higher temp. and a longer time are necessary. The addn. of Na or of Na + CO_2 is without influence. With respect to polymerization, II corresponds therefore to α- and δ-substituted butadienes, which are polymerized with more difficulty than are the meso-substituted ones. $FeCl_3$ has a powerful accelerating action. II yields a liquid and a solid polymer. That in the latter there is a rubber-like structure, a *"dihydrobenzene rubber,"* is supported by its mode of prepn., its soly., it behavior on heating, distn. and bromination, and its similarity to other artificial rubbers, particularly erythrene-rubber. Furthermore it appears in 2 modifications, which are distinguished by their soly. in Et_2O and their behavior towards Br. Milling and vulcanization tests were not made. The liquid polymer is a *dimer* of II and is, therefore, a terpene, if in this class the dimeric butadienes are included. If it is considered to be formed in an analogous way to dimeric erythrene (cf. H. and Tank, *Z. angew. Chem.* **1912**, 1465; *C. A.* **6**, 413) its formula would be (VI). It has, however, probably formula (VII), which would correspond to the heretofore accepted but in no way established formula of dicyclopentadiene. The new terpene is essentially different from dicyclopentadiene, for while the latter is solid at room temp. and is decompd. on distn. into the monomeric hydrocarbon, the new terpene does not solidify in freezing mixts. and it does not decomp. when boiled at atm. pressure. Refractometric studies gave no clue to the structure of the terpene, but did show that there is no conjugation. Its high d. and n suggest a tricyclic system. 1,2-Dibromocyclohexane, prepd. from cyclohexene and Br in $CHCl_3$, b_8 96°, b. 222–4° (evolution of HBr), is a strongly refractive liquid, with slight odor, reverts to cyclohexene by the action of Mg in Et_2O; it is not very reactive, but reacts under pressure with exchange of its Br atom and with sepn. of HBr, in all the cases studied, Δ^2-tetrahydrobenzene derivs. being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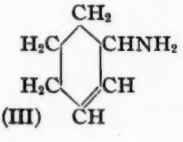
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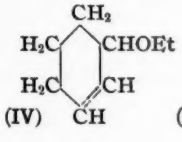
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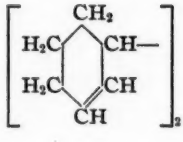
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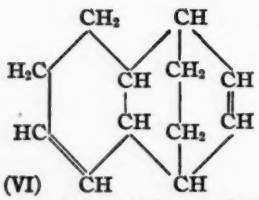

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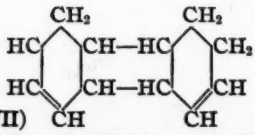

(VII)

formed. By heating it 10 hrs. at 100–120° with 20% alc. NH_3 in an autoclave, evapg. the filtrate *in vacuo*, shaking with dry KOH, extg. with Et_2O, distg., the 135–54° fraction, neutralized with dil. H_2SO_4 (to sep. any IV formed), IV removed by Et_2O, and the product sepd. with alkali, there was obtained 50% of III, unpleasant odor, b. 137–8°, strongly refractive. Neutralized with H_3PO_4 soln., it forms a *phosphate* $C_6H_{11}N.H_3PO_4$, sinters 150°, m. 158°, yields about 70% of II when dry-distd. in CO_2. Dibromocyclohexane boiled 2 hrs. with NaOEt soln., and distd. yields II and IV. The latter must be distd. repeatedly over Na until it is free of Br. IV then b. 154–5° and, like II, with EtOH concd. H_2SO_4 (equal parts) gives a blue-red coloration. It is unaltered by heating in a tube at 300°, but it is attacked in some unexplained manner by boiling dil. H_2SO_4, and is oxidized to succinic acid by boiling HNO_3. *Dibromide*, $C_8H_{14}OBr_2$, oil with peculiar odor, b_9 131–2°, strongly refractive, stable toward $KMnO_4$. IV treated with dil. aq. $KMnO_4$ with addn. of ice, filtered *in vacuo* and evapd. in CO_2, yields *1-ethoxy-2,3-dihydroxycyclohexane*, $C_8H_{16}O_3$, m. 27–8°. IV heated with 5% of its wt. of $KHSO_4$ at 170–5°, distd., the distillate redistd. with $KHSO_4$, the EtOH removed with water, and distd. over Na in a current of CO_2, yields II, odor suggesting leeks, b. 80.5–81°, d_4^{20} 0.8410, n_D^{20} 1.4755, n_γ^D 1.4951, gives a raspberry or violet-red color with alc. H_2SO_4, becomes resinous with concd. H_2SO_4 and is oxidized by HNO_3; *tetrabromide*, prepd. with Br in $CHCl_3$, m. 87–8°; with boiling NaOEt soln. it forms PhBr. Passing SO_2 through II in Et_2O forms the *addn. compd.* $C_6H_8O_2S$, on dry distn. gives 50–60% of II, some VI and products contg. S. II adds only 1 mol. of H halide, giving Δ^2-derivs. Passing HCl through II in AcOH at 0° forms *1-chloro-Δ^2-tetrahydrobenzene*, hygroscopic oil with pleasant odor, b_{40} 65–6°; with boiling NaOEt soln. it gives II and IV. *1-Bromo-Δ^2-tetrahydrobenzene*, b_{40} 80–2°, gives with NH_3 or $NHMe_2$ in C_6H_6 a mixt. of III and 1-dimethylamino-Δ^2-tetrahydrobenzene. Dibromocyclohexane or 1-chloro-Δ^2-tetrahydrobenzene and AcOK boiled 48 hrs. or 1 hr., resp., with AcOH yield *Δ^2-cyclohexanol acetate*, fruit odor, b. 180–2°, oxidized by $KMnO_4$, gives with alc. H_2SO_4 an intense blue-red color, is unaltered at 300°, while its Δ^1-isomer does not show the color reaction and on heating decomps. into AcOH and a hydrocarbon. Boiled with alc. KOH *in vacuo* and then distd. at ordinary pressure it yields *Δ^2-cyclohexenol*, oil with faint odor, b. 161–3°, does not give the reactions of ketones, with alc. H_2SO_4 gives the same color as the acetate, and with a little H_2SO_4 in EtOH it forms IV. 1-Bromo-Δ^2-tetrahydrobenzene and a little C_2H_5Br boiled with Mg in Et_2O for 1 hr. yields *$\Delta^{2,2'}$-dicyclohexene* (V), oil with odor of Ph_2, b. 230–2°, b_8 103°, gives with alc. H_2SO_4 a deep blue-red color. *Tetrabromide*, from Br in AcOH, m. 154–5°, gives no color with alc. H_2SO_4, when heated it evolves HBr and leaves a residue which gives a blue-red color with alc. H_2SO_4. *Polymerization of $\Delta^{1,3}$-dihydrobenzene.*—II heated in a tube at 200–20° for 10 hrs. and the thick, milky liquid distd. yields 0–8% of unaltered II, 55–65% of terpene and 40–30% of *rubber*. At 120°, heating for 30 days is necessary. Below this temp. II does not change materially. For the polymerization of large quantities, 800 g. of II was heated 2 hrs. at 200° in a Cu autoclave and after fractionation the crude rubber was dissolved in $CHCl_3$. Addn. of this $CHCl_3$ soln. to 10 times its vol. of Me_2CO pptd. *dihydrobenzene rubber*. After boiling off the terpene from the product above, the crude residue (protected from oxidation) can also be treated with concd. NH_4OH and steam-distd. until oil no longer collects. Further purification of the products from both processes by $CHCl_3$ and EtOH gives a white, odorless *powder*, which sinters about 75°, becomes vitreous at about 90° and at about 105° forms opaque droplets. When freshly prepd. it is sol. in C_6H_6 and $CHCl_3$ and insol. in EtOH, Me_2CO and glacial AcOH, oxidizes in the air (absorbing $1O_2$) and cannot be analyzed with precision. When its $CHCl_3$ soln. is poured into EtOH, only part seps. as a gel. This *Et_2O-insol. rubber*, after pptn. from $CHCl_3$ by EtOH, is a white powder, which sinters around 100°, but forms no droplets, is especially readily oxidized and becomes highly electrified on being rubbed. The *Et_2O-sol. rubber* is obtained by pouring Et_2O soln. into EtOH, and forms white flakes, which on heating behave like the original product. There was about 3 times as much Et_2O-sol. rubber as Et_2O-insol. rubber. When II is poured on a little $FeCl_3$, lively boiling ensues and soon a thick

oil collects at the bottom. Preferably, however, $FeCl_3$ in Et_2O and II in Et_2O are mixed, whereupon boiling soon ensues and a dark blue sirup seps. When solns. of this sirup in Et_2O and in $CHCl_3$, after washing with water, were poured into EtOH, the product resembled the polymerization product obtained by heating, but the ratio of Et_2O-sol. to Et_2O-insol. part was reversed. Decompn. of the dihydrobenzene rubber by heat was similar to that of natural rubber. On distn. at atm. pressure, 40 g. yielded 29 g. of distillate, from which II and VI were isolated. On dry distn. *in vacuo* (12 mm. Hg), the chief product, above 240°, was a yellow *oil* with green fluorescence. Towards Br in $CHCl_3$, dihydrobenzene rubber behaved like other rubbers. The Br absorbed indicated that a part added $1Br_2$ and another part $2Br_2$. The Et_2O-sol. rubber prepd. with $FeCl_3$ furnished a *dibromide* $C_{12}H_{16}Br_2$, white powder when pptd. from $CHCl_3$ by EtOH, decomps. 210–15°. The Et_2O-insol. rubber prepd. with $FeCl_3$ furnished a *tetrabromide*, $C_{12}H_{16}Br_4$, turns brown at 350°. The analyses of these bromides were doubtful. *Dimeric dihydrobenzene*, $C_{12}H_{16}$ (VI). The crude terpene was purified by distn. *in vacuo*, the last distn. over Na. It was an oil with odor of pine needles, highly refractive, b_3 86–7°, b. 229–30°, d_4^{14} 0.9951, n_D^{14} 1.5288, n_γ^{14} 1.5487, easily oxidized in the air to a thick, odorless *oil*, is resinified by concd. H_2SO_4 and HNO_3, is slowly oxidized by $KMnO_4$, gives with alc. H_2SO_4 a raspberry-red color and with AcOH contg. a little H_2SO_4 a violet color, in $CHCl_3$ it adds $2Br_2$ readily but the *Br addn. product* could not be isolated, and it also forms a *HCl-addn. product*. AcOH satd. with HCl added to VI and $AmNO_2$ in AcOH in the cold forms the *bisnitrosochloride*, $C_{24}H_{32}O_2N_2Cl_2$, m. 132–3°. C. C. DAVIS

Direct uses of waste rubber. JOSEPH ROSSMAN. *India Rubber World* **77**, No. 6, 60–1(1928).—A list of 56 American and foreign patents with brief descriptions of their contents. C. C. DAVIS

Rubber physical testing. E. R. BRIDGWATER. *India Rubber World* **77**, No. 6, 57–9(1928).—An illustrated description of the app. and methods used in the labs. of the du Pont Co. C. C. DAVIS

Rubber compounding practice. WEBSTER NORRIS. *India Rubber World* **77**, No. 4, 57–8; No. 5, 58–60; No. 6, 65–6(1928); cf. *C. A.* **22**, 333.—The use of *"thermatomic" C, clays, Zn oxides, Mg carbonate, glue, C black* and *lampblack* are described, with representative formulas of rubber mixts. contg. them. C. C. DAVIS

Further data on tackiness in crude rubber. O. DE VRIES AND N. BEUMÉE-NIEUWLAND. *Arch. Rubbercultuur* **11**, 557–66(1927). (In English 567–72); cf. *C. A.* **19**, 3615.—The expts. of Groenewege (*Arch. Rubbercultuur* **8**, 641(1924)) do not prove that tackiness is accompanied by loss of N and a further sample is cited by de V. and B.-N. to show that there is no simple relation between a tendency to become tacky and a low N content before or after its onset. Moreover, exception is taken to the conclusion of G. that papain induces tackiness and rubber coagulated with papain may have excellent aging properties, at least when preserved in darkness. *Rubber coagulated with HCl* gradually becomes tacky and finally completely resinous, even when preserved in darkness, but light accelerates this deterioration. This change can be followed by detns. of the plasticity and viscosity. Traces of Cu salts also cause tackiness and ultimate resinification. Sunlight causes tackiness and weakening, which ceases when the rubber is put in darkness. Here, too, the progress of these changes may be followed by changes in the viscosity and plasticity, particularly in the early stages. C. C. DAVIS

The mercury vapor lamp. Its uses in a rubber factory. P. G. NAGLE. *Trans. Inst. Rubber Industry* **3**, 304–11(1927).—Pigments may appear white in ordinary daylight and yet exhibit a characteristic color when viewed in ultra-violet light filtered through a Chance screen (chiefly wave lengths of 3300–3900). Moreover, samples of the same pigment from different sources may vary widely in color under ultra-violet light. ZnO and lithopone are good examples of this. In an examn. of 8 grades of ZnO mixed with glycerol, none of which could be distinguished in daylight, 1 appeared light green, 1 light gray-green, 1 light green-gray, 2 orange-buff, 1 bright apple-green, 1 pale dull violet and 1 (chem. pure ZnO) deep violet. On the other hand after 10 min. at white heat, all Zn oxides were green. The same distinctive shades were visible in rubber mixts. when a small proportion was cured with rubber contg. S, accelerator and lithopone. Even when these rubber mixts. were made dark gray by C black, the individual Zn oxides could still be distinguished. The same phenomena were true of lithopones, though the range of colors was not so great. Thus 16 samples appeared deep violet, pale violet, brown or almost white. An examn. of rubber imperfectly mixed with ZnO and lithopone revealed the characteristic colors of the 2 pigments, indicating the possibility of detg. the *distribution of powders in rubber mixts.* The lithopones which appeared deep violet were the most nearly sunproof, and those which appeared white darkened the most rapidly. In filtered ultra-violet light, however, these latter were resistant,

indicating that the radiation responsible for the darkening is of shorter wave length than that transmitted by the Chance screen. In filtered ultra-violet light, mineral oils and vaseline were fluorescent and phosphorescent, coal tar showed a faint yellow-brown fluorescence and S assumed a bronze color, and in the form of "bloom" can be readily distinguished by this method. Addn. of 1% coal tar to a black rubber mixt. changed its appearance in filtered ultra-violet light from very dark violet to gray-blue. Many other inorg. and org. substances showed characteristic colors when viewed in filtered ultra-violet light (cf. Cappelli, *C. A.* **22,** 1197) and these were visible under various conditions. Thus various tire sections appeared violet, brown-violet, blue, green, yellow and brown-red. The expts. show the potential value of *ultra-violet light for the examn. of materials and substances to control uniformity and to study differences in compn.* A general discussion follows the paper. C. C. DAVIS

Tests for rubber tiling. J. H. STEDMAN. *India Rubber World* **77,** No. 5, 61–2 (1928).—The tests include *tensile strength, abrasion* and *water absorption.* C. C. D.

Rubber and the army gas masks. A. A. FRIES. *India Rubber World* **77,** No. 6, 67–8(1928). C. C. DAVIS

Variation of color in carbon black. C. R. JOHNSON. *India Rubber World* **77,** No. 5, 65–6(1927).—A large no. of C blacks were examd. to det. whether there is any relation between the color and the quality imparted to rubber. The expts. show that C blacks of different colors may have the same effect in cured rubber, and that no source of supply produced a C black of uniform quality as judged by tensile strength, modulus and rate of vulcanization. Those C blacks which impart the poorest quality to rubber have the greater depth of blackness. An instrument for detg. the color of C black is described and illustrated, termed a *nigrometer,* which follows the principle of the intensimeter and measures comparatively the quantity of light reflected from the C black. It distinguishes the colors of 2 C blacks which appear alike to the unaided eye. C. C. DAVIS

Notes on rubber manufacture. T. E. H. O'BRIEN. *Trop. Agr.* (Ceylon) **69,** 197–201(1927).—Expts. indicate that it would require 15 yrs. for formic acid of twice the strength necessary for rubber coagulation to corrode through a good grade of Al coagulation pan. The enameled iron ones now in general use are of short life due to chipping. A. L. MEHRING

Rubber inventions and processes. ANON. *Bull. Rubber Growers' Assocn.* **10,** 27–8(1928).—Nine British patents are described. C. C. DAVIS

The theory of needle-shaped rubber molecules in science and in practice. E. LINDMAYER. *Gummi-Ztg.* **42,** 1025–8(1928).—A further discussion of the theory of needle-shaped rubber mols. (cf. *C. A.* **21,** 3487), examples being cited to show that the theory is of aid in explaining colloid-chem. facts. C. C. DAVIS

Microscopy in the service of the latest developments in plantation technology. E. A. HAUSER. *Kautschuk* **1928,** 3–5.—An address dealing with the potential value of the microscope in studying the *formation of latex,* its characteristics and *coagulation* phenomena. C. C. DAVIS

Changes in methods and treatment of materials possible by application of the theory of antioxygens. J. DUGUÉ. *Compt. rend.* **185,** 389–91(1927).—Among the sugars, resins, proteins and other substances in rubber latex, some have as great an affinity as the rubber for O and therefore have an antioxygen power in their ability to protect the rubber component from oxidation. With present methods of collecting latex, absorption of O cannot be prevented, and an antioxygen should be added to the latex immediately. To avoid a possible deficiency or to offset partial destruction of the natural antioxygens present, concn. *in vacuo* would be of advantage as a means of removing nearly all the O, and at the same time this process would permit advantage to be taken of the original plasticity of the rubber. The phenomenon of *autoöxidation* with its ensuing polymerization permits of an interpretation of *aging* if it is assumed that the polymers no longer have the elasticity of rubber and are rigid and brittle, particularly when cold. During vulcanization the S first combines with the rubber and then causes it to polymerize, which is similar to the action of O in the cold. With the temp. and pressure of hot vulcanization, polymerization takes place subsequently and elastic rubber is regenerated. This action is hastened by accelerators, which have both an antioxygen and an "anti-sulphur" action, insofar as they suppress instead of promote polymerization. Since, however, vulcanization is carried out under pressure, the O in the mass is not eliminated and it resumes its function of catalyzing the polymerization, *i. e.,* the aging of the rubber. Hence if a suitable treatment could be devised for preventing autoöxidation aging would not take place. A. P.-C.

Large mixing machines and their proper use in rubber and cable factories. WERNER ESCH. *Kautschuk* **1928,** 16–22.—The technic of mixing in machines of the Banbury

type is described, with typical batches which can be economically mixed by this method.
C. C. DAVIS

Leather factice. RUDOLF DITMAR. *Gummi-Ztg.* **42,** 913(1928); cf. *C. A.* **21,** 4098.—Brown and white factices were prepd. by first mixing the oils with leather dust and then treating with S and S_2Cl_2, resp., in the usual way, representative formulas being used. Cured rubber contg. leather factice prepd. with S_2Cl_2 behaved on aging the same as the corresponding mixts. contg. no leather. C. C. DAVIS

Testing of insulating (friction) tape, with special reference to its tackiness and stability. MARTIN KRAHL. *Gummi-Ztg.* **42,** 965–9(1928).—A method and technic for detg. the tackiness and aging of tape under standardized conditions are described and illustrated. The tape is rolled up under tension and the continuous stress required to unroll it at a const. speed is then recorded graphically. The length of the fibers may also be measured (cf. Ditmar, *C. A.* **19,** 3386). Tape is aged by exposure to ultraviolet light, the app. allowing uniform exposure by means of a rotating drum carrying the tape. The deterioration is judged by measuring the tackiness by the method described, before and after aging under standard conditions. C. C. DAVIS

Testing of the adhesiveness of rubberized tape. LOTHAR HOCK. *Gummi-Ztg.* **42,** 1028(1928).—Comments are made on testing methods described by Krahl (cf. preceding abstr.). The principles embodied in the method are not new and except for the machine used, the same test has been used by Hock (cf. *C. A.* **18,** 3740).
C. C. DAVIS

The technic of vulcanization. A. M. MUNRO. *Chem. Eng. Mining Rev.* **20,** 98–103(1927).—A general review, with the inclusion of new data on the *penetration of heat through tires during vulcanization* and the temps. after different times in various parts of the tire. The results show that the rise of temp. usually employed can be considerably shortened, *e. g.*, under the conditions tested, a straight rise of 30 min. to the curing temp. would be as effective as 15 min. up to 260° F., 25 min. to 260° F. and 5 min. to 294° F., saving 15 min. of the curing time. The technic used in obtaining these data is described. C. C. DAVIS

New methods of vulcanization. A. BRINTET. *Rev. gén. mat. plastiques* **3,** 585–90, 652–4(1927).—A brief description of some of the most recent processes of vulcanization.
A. PAPINEAU-COUTURE

The reactions of aniline and its homologs as accelerators of vulcanization. TAKEO KIMISHIMA. *Mem. Coll. Eng. Kyushu Imp. Univ.* (Japan) **4,** 193–250(1927).—In studies in recent yrs. of the mechanism of acceleration, there has been almost no attention paid to the action of $PhNH_2$ (I) and its derivs. For this reason the *reaction products of accelerators and S* and the *effect of these products on vulcanization* were studied experimentally. By heating I and S at 160–70° for several hrs. (cf. Hofmann, *Ber.* **1894,** 2807, 3320) a large proportion of *o*-diaminophenyldisulfide (II), a small proportion of *o*-diaminophenylmonosulfide (III) and about 10% of *p*-diaminophenyldisulfide (IV), m. 78° (cf. 80° of Hofmann, *loc. cit.*), were formed and H_2S was evolved. A *resin* was also formed, and though it could not be crystd. its analysis approached $C_{12}H_{12}N_2S_5$ and it was probably a *polysulfide*, perhaps in part a pentasulfide. III is formed by thermal decompn. of II. Since II was the chief product, its action as an accelerator was studied. In all comparisons, the % combined S under definite conditions was used as a criterion of rate of vulcanization. Vulcanized in air at 143.5°, II does not accelerate a rubber-S mixt. (perhaps because of decompn. of II), whereas a similar rubber-S mixt. contg. I evolves H_2S. Therefore the rubber-S mixt., the same mixt. contg. I and the same mixt. contg. II were vulcanized in air, in CO_2 and in H_2S. In air and in CO_2 the mixt. contg. I vulcanized more rapidly than did a similar mixt. contg. III, but in H_2S the mixt. contg. II vulcanized much more rapidly than did the mixt. contg. I. The vulcanization coeff. of the mixt. contg. II was 4–5 times as great in H_2S as in air or CO_2. This showed that II accelerates only with H_2S. When H_2S is passed for a long time into hot acidic II, the latter is reduced to *o*-aminothiophenol (V), thus: II + $H_2S \longrightarrow$ V + S, and V is reoxidized to II by air or by fusion with S. This suggests a mechanism of acceleration by I. I and S form II, II is reduced by H_2S to V and the nascent S reacts with the rubber. V is reoxidized by S to II and H_2S, the cycle being repeated. This means that rubber can be vulcanized with II and H_2S and that V is an accelerator. Tests showed that rubber and II vulcanize very slowly in H_2S. Rubber-S-V mixts. vulcanized in air at the same rate as similar rubber-II mixts. in H_2S. Further tests in which rubber-V mixts. were vulcanized with different proportions of S showed that V is a powerful accelerator when excess S is present but with smaller proportions of S it is without action and with still less S it retards vulcanization. This suggests a relation between acceleration and formation of a polysulfide. Therefore rubber was heated with and without S and with the resin from the I-S fusion mixt.

(*loc. cit.*). With S and in H_2S, the polysulfide resin accelerates about the same as **II**, and even without S in H_2S the polysulfide resin brings about vulcanization. The mechanism with **I** is assumed to be: (1) $I + S \longrightarrow V$; (2) $2V + xS \longrightarrow (C_6H_4NH_2)_2S_{x+1} + H_2S$; (3) $(C_6H_4NH_2)_2S_{x+1} \longrightarrow (C_6H_4NH_2)_2S_2 + (x - 1)S$(active) and (4) $(C_6H_4NH_2)_2S_2 + H_2S \longrightarrow 2V + S$(active). The activity of **I** is decreased by ZnO, because ZnO absorbs H_2S and thus indirectly prevents the action of **II**, and because it favors the formation of **III**. Further vulcanization tests showed that **IV** is a more active accelerator than **II**, and unlike **II**, **IV** is active in air and in CO_2, for which there is no definite explanation. In air or in CO_2, **III** is about as active as **II**, but in H_2S it is far weaker than **II**. In general the same phenomena are true of PhNHMe (**VI**), $PhNMe_2$ (**VII**) and *p*-$MeC_6H_4NH_2$ (**VIII**). **VI** and S heated together yielded dimethyldiaminophenyldisulfide (**IX**) and methylaminophenylmercaptan (**X**), while **VII** and S yielded tetramethyldiaminophenyldisulfide (**XI**) and benzothiozolemethenedisulfide (**XII**) (cf. *Ber.* **21**, 59(1888)), **IX** and **XI** being formed in very small proportions. With H_2S, **IX** and **XI** are active accelerators and they are reduced by H_2S to the corresponding thiophenols, which in turn are oxidized by S to **IX** and **XI**. **XI** has an accelerating action even without H_2S. With H_2S, **X** and **XII** have no accelerating action, and in air or in CO_2 they retard the rate of vulcanization. Prolonged heating of **VIII** and S (50:23) at 160° gave chiefly bis-[5-methyl-2-aminophenyl]disulfide (**XIII**) with a small proportion of bis[5-methyl-2-aminophenyl]monosulfide (**XIV**) (cf. *Ber.* **4**, 392(1871); Bogert and Mandelbaum, *C. A.* **18**, 1822). With PbO present, the chief product is **XIV**. Since bis-[2-methyl-5-aminophenyl]disulfide (**XV**) and dehydrothio-*p*-toluidine (**XVI**) have also been isolated from the reaction of **VIII** and S, **XIII**, **XIV**, **XV** and **XVI** were tested for their accelerating action. With H_2S, **XIII** is a powerful accelerator, but with air or CO_2 it is inactive. **XV** is a powerful accelerator in air, CO_2 and H_2S, its activity being particularly great in H_2S. Both **XIII** and **XV** are reduced by H_2S to the corresponding aminothiophenol, which can then be oxidized to **XIII** or **XV** by S or O. **XIV** and **XVI** are less active than **XIII** and **XV**, and furthermore it is probable that in the conditions prevailing during vulcanization practically none of either is formed. **VIII** therefore accelerates because of the formation of **XIII** and H_2S or 5-methyl-2-aminothiophenol as a reduction product. The mechanism of acceleration by **I** is therefore applicable to **VIII**. **I** and **VIII** are also similar in that the activity of their monosulfides is not increased so greatly by H_2S as is that of their disulfides. Following the method of Williams and Beaver (*C. A.* **17**, 1559), the thermal effects during vulcanization with **I**, **II**, **III**, **IV**, **VI**, **VII**, **VIII**, **IX**, **XI**, **XIII**, **XIV** and **XV** were detd. In preliminary tests there was no significant heat evolved when rubber-accelerator, S-resin or S-accelerator was heated. With rubber-S-accelerator, there was no excess temp. when 145° and 155° were used, but at 165° or above, the more active the accelerator the higher was the excess temp. of the mixt. Therefore the *relative activity of accelerators* can be detd. by measuring the rise in temp. of rubber-S-accelerator mixts. heated at 175°. At least, around 145° the action of an accelerator is chem. and not thermal. Tensile strength and elongation tests of the mixts. contg. the various accelerators conformed to the coeff. of vulcanization detns. in showing the relative activity of the various compds. Because H_2S is necessary for the max. activity of the disulfides, they are not promising as com. accelerators. **IV** and **XV** are very active and increase the tensile strength of rubber-S mixts. without ZnO, whereas the other sulfides are practically inactive without ZnO. Without ZnO, **XV** is slightly less powerful than aldehyde-ammonia and more powerful than hexamethylenetetramine, while **IV** is slightly more powerful than hexamethylenetetramine. With ZnO, **XIII** and **II** greatly improve the strength of cured rubber, **XIII** behaving about the same as hexamethylenetetramine and **II** about the same as thiocarbanilide. **II**, **IV**, **XIII** and **XV** may be of com. value, for they are harmless to workers and impart no odor to the cured rubber.

C. C. Davis

Polymerization and rubber. J. R. Katz, J. Selmann and L. Heyne. *Kautschuk* **1927**, 215–22; *Brit. Chem. Abstracts* **1927B**, 610; cf. *C. A.* **21**, 1730, 3766.—Stress is laid on the desirability of investigating, as a means of explaining mol. structure, not only cryst. interference phenomena but also the amorphous rings resulting from the influence of various substances on x-rays. The mathematical relation, indicated earlier by Keesom, between the diam. of the amorphous ring and the mol. vol. does not hold for many polymerized tung oils and synthetic rubbers. For each of these the diam. of the outer amorphous ring is almost identical with that of the corresponding unpolymerized substance. From the equality of the values for synthetic rubbers and the corresponding butadiene, it is possible to identify the chem. origin of a synthetic rubber. Polymerization, however, sometimes gives rise to a second ring of smaller diam. On ascending a homologous series, *e. g.*, alcs. or fatty acids, the mol. vols. indi-

cated by the amorphous ring approach a const. value. These mol. vols. also approach more closely to the expected value of a ring compd., such as C_6H_6, than of a corresponding open-chain compd., *e. g.*, hexane. Keesom's law does not, however, hold true with many substances, and apparently the more symmetrical or compact the mol. the more exact is the law. Though $HNEt_3$ gives only 1 ring, the tri-Pr, tri-iso-Bu and tri-iso-Am bases show 2 rings, the inner of which approximates Keesom's law. This is also true of certain ortho esters and paraldehydes. In such cases the dimensions of the outer ring seem to be related to the magnitude of the side chains of the mol. In general the results indicate that in many cases where a mol. is composed of several similar groups, 2 amorphous rings appear, the inner one of which in its relation to the mol. vol. agrees with Keesom's law. With certain colloidal substances obtained by polymerization, rings of smaller diam. indicative of cryst. components of high mol. wt. are observed in addn. to the amorphous rings. C. C. DAVIS

Phenomena involved in the stretching by raw rubber. E. A. HAUSER AND P. ROSBAUD. *Kautschuk* **1928,** 12–4.—The expts. had as their ultimate object the correlation of phenomena observed when rubber is stretched with x-ray observations and with thermodynamic principles. The relations between the ultimate elongation and the temp. and between the ultimate elongation and the rate of extension were first studied. With decrease in temp., the tensile strength increased greatly and the ultimate elongation diminished greatly until at —185° there was no elongation and the strength was a max. The greater the rate at which rubber was stretched the greater were its ultimate elongation and its tensile strength. These results are shown graphically, including a 3-dimensional model to show the tensile strength as a function of temp. and of rate of stretching. At —185° rubber showed a max. tensile strength and no elongation, while at 80° under a min. rate of extension it showed a max. elongation, but no strength. When rubber was stretched isotropically, the x-ray interferences which ordinarily appear at 80–100% extension did not become visible even at 500% extension. The proportionality between the intensity of the point interferences and the elongation was true only when the rate of extension was maintained const. The appearance of interference phenomena at 80–100% extension represents a lower limit, and the slower the rate of extension the higher is the % extension at which interference appears. It should, however, be possible by proper choice of temp. (*e. g.*, —20°) and with an extremely high rate of extension to lower the min. extension at which interferences appear to a lower limit. By means of a special calorimeter where the heat tone of rubber being stretched could be followed, it was found that no heat tone was evident when the rate of extension was slow. As the rate increased, a heat tone was detected, and the greater the rate the greater the heat tone. Furthermore, as with x-ray interferences, there was a linear relation between the heat and the degree of extension only when a const. rate of extension was maintained. There is probably a close relation between x-ray interference phenomena and the Joule heat effect. C. C. DAVIS

Aging of stretched rubber. ARTHUR KELLY, B. S. TAYLOR AND W. N. JONES. *Ind. Eng. Chem.* **20,** 296–8(1928).—Samples representative of a wide variety of rubber goods were aged in the normal state and under varying degrees of elongation in sunlight. In some cases a comparison was made with aging in the normal state in ultra-violet light, the 70° air oven and the O-bomb. No direct relation was found between the results of aging in sunlight and by the other methods, but certain conclusions may be drawn. In sunlight, ultra-violet light and the 70° oven, stretching accelerated the rate of deterioration (no data were obtained in the O-bomb), but the rate of deterioration was not proportional to the degree of elongation. During the early stages in sunlight there was a crit. elongation at which deterioration was most rapid in each case, but later the greater the elongation the faster the deterioration. The results are given in detail in tables and graphs. C. C. DAVIS

Effects of ozone on stretched rubber. F. H. HAUSHALTER, W. N. JONES AND J. W. SCHADE. *Ind. Eng. Chem.* **20,** 300–2(1928).—The same phenomena which were evident when vulcanized rubber mixts. were stretched and were exposed to sunlight (cf. preceding abstr.) were observed when the stretched samples were exposed to air contg. O_3. The effect of O_3 was so severe that when they were elongated only 0.1% they cracked in a few min. As in sunlight during the earlier stages of exposure, cracking was greatest at an intermediate crit. elongation. Stretching was not accompanied by an immediate increase in hardness, and only when a crit. elongation was reached did the hardness increase with increasing tension, and the effect of O_3 diminish correspondingly. In the normal state (unstretched) the samples were far less sensitive to O_3, and after many hrs. cracking did not occur. Phys. tests did not indicate a decline in quality. In conjunction with tests in sunlight (cf. preceding abstr.), the tests suggest a relation between the progressive changes in sunlight and in O_3. C. C. D.

The electrolytic precipitation of fresh and of preserved latexes and the part played by protein in the coagulation. P. SCHOLZ. *Kautschuk* **1928,** 5–8.—The expts. deal with (1) the influence of the concn. of latex on the coagulation value; (2) the influence of protein on coagulation, through comparison of the coagulation value of fresh latex with deproteinated latex and with milk and (3) the difference between fresh and preserved latex. The coagulation value was considered to be the min. concn. of electrolyte which would cause coagulation where equal vols. of electrolyte and latex were mixed under standard conditions. The coagulation values of KCl, LiCl, $BaCl_2$, $MgCl_2$, $MgSO_4$ and $NiSO_4$ did not change with diln. of the latex, whereas those of $CuSO_4$, $Al_2(SO_4)_3$, $La(NO_3)_3$ and AcOH diminished to 0.1 their value when the latex was dild. 50-fold. These last 4 compds. are also excellent coagulants of protein, as shown by coagulation of milk where again the notable influence of concn. was manifest. This supports the theory that protein is a *protective colloid in latex*. Comparative tests of fresh latex, deproteinated latex (cf. Pummerer and Pahl, *C. A.* **22,** 885) and milk showed that the latter is a typical hydrophobic sol in which diln. has no influence on the coagulation value, and that latex is a hydrophobic sol which is strongly protected by protein against univalent electrolytes but which is relatively sensitive to bivalent electrolytes. Neutralization of latex preserved with KOH and soap ("Revertex") did not alter the coagulation values, whereas neutralization of latex preserved with NH_3 made it much more sensitive than before to strong coagulants of protein. On the other hand, NH_3-preserved latex, particularly when dil., was less sensitive to bivalent solns. after neutralization than before. The coagulation values of neutralized sols were around 150% higher than those of fresh latex, except for $MgSO_4$ and acids, but toward $MgSO_4$ preserved latexes were very stable (400–1500% higher) and toward acids "Revertex" was very stable. The general high coagulation values of preserved latexes depend upon the protective colloid added to "Revertex" and upon the stabilization of the protein by the addn. of the OH ion to NH_3-preserved latex. The great stability toward $MgSO_4$ is perhaps to be ascribed to the solvation influence of the SO_4 ion at neutralization and to the strong hydration of the Mg ions. "Revertex" and NH_3-preserved latexes were filtered through an ultra-filter and the coagulation value of the sera was detd. in comparison with milk and with egg albumin sol. "Revertex" serum was neutral (to bromothymol blue) whereas NH_3-preserved latex serum was alk. A comparison of the coagulation values of the sera of NH_3-preserved latex and of "Revertex" with those of egg albumin and milk showed the relatively powerful influence of the preservative, so that the protective proteins can be characterized only by an investigation of ultra-filtered fresh latex.
C. C. DAVIS

Color reactions of rubber. H. PAULY. *J. prakt. Chem.* **118,** 48–52(1928).—Except where its insoly. interferes, rubber gives the reactions of Hesse (*Ann.* **192,** 178(1878); **211,** 283(1882)), of Liebermann (*Ber.* **18,** 1804(1885)), of Burchard (*Chem. Zentr.* **1890,** I, 25), of Chugaev (an eosin color when warmed with AcCl and $ZnCl_2$ in AcOH), of Chugaev-Golodetz (*C. A.* **2,** 1626) and of Kahlenberg (*C. A.* **16,** 2315). These reactions are shown by wild and plantation rubbers, by purified rubber and by synthetic rubber, so that the reactions are characteristic of the rubber hydrocarbon and not of its non-rubber components. The color obtained in the Burchard reaction depends upon the type and purity of the rubber, the best natural and synthetic rubbers giving the clearest reaction. Rubber purified with NaOH gives a stable red color and ppt. without the subsequent color changes, perhaps because the latter depend upon oxidation products. This idea is supported by the fact that amyrins, which are present in natural rubber, also give in the Burchard reaction a purple color, without a color change. The addn. of a little benzoyl peroxide brings about a color change with amyrins but not with purified rubber, indicating that natural rubber already contains resinous oxidation products. Na-rubber does not give a definite Burchard or Liebermann reaction. In the Chugaev-Golodetz reaction, the color depends upon the acid nature of Cl_3CCO_2H, and on diln. with water, it disappears and the rubber is pptd. apparently unaltered. This suggests a halochrome, in which case completely hydrogenated rubber would not give a color with Cl_3CCO_2H. Such color reactions have never been observed in unsatd. acyclic hydrocarbons, and the reactions of rubber indicate in conformity to the Harries theory that it has a cyclic structure. *Guttapercha* gives color reactions like those of rubber.
C. C. DAVIS

The color thermoscope and its use in the rubber industry for the determination of the temperature of rolls and of the temperature for drying raw rubber. RUDOLF DITMAR. *Gummi-Ztg.* **42,** 1133–4(1928).—At room temp. Cu_2HgI_4 is red but at about 70° it changes to brown-black, and this transformation is reversible. At room temp. Ag_2HgI_4 is canary-yellow, but at 40–50° it changes to deep orange-red, and this too is reversible. These 2 substances therefore offer a means of estg. the temp. of rolls within

the precision indicated above. For these uses, the colors are mixed with light colored shellac, and varnished paper or cardboard is coated with the mixt. C. C. DAVIS

Pigment reënforcement of reclaimed rubber. H. A. WINKELMANN AND E. G. CROAKMAN. *Ind. Eng. Chem.* **20**, 445(1928).—Correction (cf. *C. A.* **22**, 1059). H. G.

Moisture in carbon black. C. R. JOHNSON. *Rubber Age* (N. Y.) **22**, 535(1928).—When stored in a damp atm., standard 12.5 lb. bags of C black for rubber absorbed water steadily for 6 days, increasing from 1.5 to 2.5% water, and required 8 days to dry again to their original condition. The results were virtually the same whether the C black was compressed or not compressed. The data are given in tabular and graphical form. The results show the importance of storing C black in a dry atm. for some days before use, if 2.5% moisture is objectionable. C. C. DAVIS

The nature of vulcanization. III. H. P. STEVENS. *J. Soc. Chem. Ind.* **47**, 37–43T (1928); cf. *C. A.* **13**, 3039.—Expts. lead to the conclusion that there is no essential difference between raw rubber and that part of vulcanized rubber which remains uncombined with S, *i. e.*, an intimate mixt. of raw and vulcanized rubber behaves substantially the same as rubber vulcanized to a proportionately less degree. Raw rubber and vulcanized rubber cannot be intimately blended and resort was had to (1) mixing C_6H_6 sols of raw rubber and of rubber cured with S_2Cl_2 and evapg. and (2) mixing raw and vulcanized latex (Schidrowitz process) and evapg. Controls were prepd. from C_6H_6 sols of vulcanized rubber and from vulcanized latex having the same % combined S as the mixts. The C_6H_6 sols were vulcanized with S_2Cl_2. The condition of the various dried products was compared by the proportion of C_6H_6 absorbed and the proportion dispersed in C_6H_6. In case (1) the higher the proportion of S_2Cl_2 the less was the swelling and the less the proportion dispersed, the products with the same proportion of S_2Cl_2 to rubber (whether by direct vulcanization or by mixing cured and raw rubber) behaving the same in C_6H_6. Likewise in case (2) there was no marked difference in the behavior in C_6H_6 of rubber from vulcanized latex and from mixts. of vulcanized latex and raw latex when the coeffs. of vulcanization were the same. The degree of swelling and soly. depended only upon the proportion of combined S, however obtained. The phys. properties of the products from vulcanized latex and from mixts. of raw and vulcanized latexes were the same for mixts. having the same coeffs. of vulcanization, adding further evidence that the products are similar in character. The products from sols and from latex are the same only when vulcanization is carried out under identical conditions, *i. e.*, so that the dispersed rubber sulfide particles are of similar shape and distribution. The close relation between the vulcanization coeff. and the phys. properties, both when vulcanization is carried out with S alone and with S, ZnO and accelerator, show that chem. combination of rubber and S is not incidental, but governs the phys. changes occurring during vulcanization. These phys. changes depend, however, upon the condition and degree of dispersion of the rubber sulfide. The dispersion medium, *i. e.*, the raw rubber, may also undergo a change during vulcanization. Assuming then that vulcanized rubber is a mixt. of C_6H_8S or C_6H_8SCl and raw rubber, the rigid phase increases with the state of cure and protects more and more the remaining plastic rubber from dispersing in solvents. But with the same proportion of rigid phase, the phys. properties may differ, for the size, shape and distribution of the rigid phase are governed by the conditions during vulcanization, *e. g.*, the temp. and rate of combination of rubber and S (acceleration). A still more effective agent than C_6H_8S for protecting rubber from solvents is *cellulose*. Where approx. 0.5% C_6H_8S (formed in vulcanization by S alone) is necessary to render rubber insol. in C_6H_6, the addn. of only 0.25% cellulose (as viscose) to rubber is sufficient. Viscose is readily incorporated in raw or vulcanized latex. Larger proportions of cellulose reduce the swelling of rubber in C_6H_6 to low values. Cellulose-rubber mixts. behave like vulcanized rubber in solvents, but above 1% cellulose the tensile strengths increase, the ultimate elongations diminish and the permanent elongations become very high. With higher proportions of cellulose, they behave when stretched like "frozen" raw rubber, and when 25% is reached they are short and brittle. In vulcanized rubber, cellulose behaves like a fine pigment. *Glue* has somewhat the same effects as cellulose. When raw latex is coagulated in the presence of *tannic acid*, the resultant rubber is almost insol. in C_6H_6. C. C. DAVIS

Chemical unsaturation of rubbers vulcanized with polynitro compounds and benzoyl peroxide, and its possible bearing on vulcanization. HARRY L. FISHER AND A. E. GRAY. *Ind. Eng. Chem.* **20**, 294–5(1928).—Rubber was vulcanized with $C_6H_4(NO_2)_2$, $MeC_6H_3(NO_3)_2$ and benzoyl peroxide to det. whether there is a change in the chem. unsatn. of the rubber as there is in vulcanization by S. The results indicate that there is no change in unsatn., after vulcanization with any of the 3 reagents,

which cannot be attributed to normal variations (1%) in the rubber. It is possible, however, that a small proportion of O does combine with the rubber and that this is sufficient to cause the phys. changes observed, in the same way that the combination of a correspondingly small proportion of S causes marked phys. changes. The results support the theory that vulcanization involves a change in the hydrocarbon other than a change in chem. unsatn. and that chem. combination with S is a secondary and subsequent reaction which results in further changes. C. C. DAVIS

Activity of certain aryl-substituted biguanides as accelerators of vulcanization. G. B. L. SMITH AND A. J. WEISS. *Ind. Eng. Chem.* **20,** 298–300(1928).—A mixt. of rubber 100, S 10, ZnO 100, accelerator 1, vulcanized at 150° was used for detg. the activity of several aryl-substituted biguanides compared with diphenylguanidine, hexamethylenetetramine, thiocarbanilide and α-cyanoguanidine (cf. Romani, *C. A.* **18,** 1066). α-*o*-Tolylbiguanide, which was of particular promise, was also tested in several com. types of mixts. α-Phenyl-, α-*o*-tolyl-, α-*p*-tolyl- and α-3,4-xylylbiguanide were similar to hexamethylenetetramine. α,α-Diphenylbiguanide was more active than the monoaryl derivs., whereas α-naphthylguanide with only a slightly lower mol. wt. was not so active as the lower homologs, perhaps because of its instability. With the exception of α-naphthylbiguanide, the activity of all the biguanides tested varied directly with the mol. wt. of the substituent radical. α-*p*-Tolylbiguanide was more active than α-*o*-tolylguanidine, indicating that the activity decreases from the *p*- to the *o*-derivs. as with diarylguanidines. The activity of α-cyanoguanidine confirmed the results reported elsewhere (cf. Brit. pat. 201,570(1923)). Benzoxazoleguanidine was the least active of any accelerator tested, and α-naphthylbiguanide was the only one which manifested an odor during milling and vulcanization. Like diarylguanidines, biguanides are relatively inactive in the absence of ZnO. In general the relations between chem. compn. and activity were about the same as with other series of accelerators (cf. Sebrell and Boord, *C. A.* **18,** 1925; Elley and Powers, *C. A.* **21,** 511; Naunton, *C. A.* **19,** 2425). C. C. DAVIS

New process for curing cord tires and molded tubes. H. R. MINOR. *Ind. Eng. Chem.* **20,** 291–4(1928).—The new process is based on extensive experimentation and possesses the advantages of the air-glycerol and the hot-water processes, with none of their disadvantages. The pressure is built up to a predetd. point with CO_2, and then steam at a pressure higher than that corresponding to the temp. desired is introduced. The steam heats the CO_2, causing it to expand, and diminishing the partial pressure of the steam which can enter. The internal temp. required is maintained const. and the conditions can be calcd. beforehand. The CO_2 precludes any chance of oxidation and it also acts as an automatic valve to control the quantity of heat added. The CO_2 may be recovered. The time of vulcanization is reduced and the quality of the products is superior to that by other processes. C. C. DAVIS

The sedimentation analysis of fillers. FRITZ EVERS. *India Rubber Tire Rev.* **28,** No. 2, 30, 33–4, 36(1928).—An English version of *C. A.* **21,** 1374. C. C. D.

Modern aspects of rubber cultivation. C. H. WRIGHT. *J. Roy. Soc. Arts* **76,** 455–506(1928). E. H.

The coloring of rubber. R. L. DUPONT. *Rev. gèn. mat. plastiques* **4,** 175–9(1928).—A brief outline is given of the testing of pigments and dyes used for coloring rubber. A. PAPINEAU-COUTURE

The wastes of the rubber manufacturing industries. J. B. C. KERSHAW. *Ind. Chemist* **4,** 115–7(1928).—A review of literature and patents on the reclaiming and utilization of waste rubber. E. H.

American rubber factories. F. KIRCHHOF. *Kautschuk* **1928,** 35–9.—An abridged version of a recent address by van Rossem (*The American Rubber Industry and Its Scientific Research Work*). C. C. DAVIS

Twenty years' work on the synthesis of rubber. FRITZ HOFMANN. *Gummi-Ztg.* **42,** 1190–2(1928).—A review. C. C. DAVIS

Patent review. C. BÖHM. *Kautschuk* **1928,** 43–4.—Recent American and foreign patents on latex, raw rubber, mixing, vulcanization and the manuf. of rubber are itemized. C. C. DAVIS

The coagulation of latex. PAUL BARY. *Rev. gén. caoutchouc* **1928,** No. 39, 3–5.—A crit. review of recent experimentation and hypotheses, with 17 references. C. C. DAVIS

Some data on rubber from Ficus, Castilloa and Manihot. O. DE VRIES AND W. SPOON. *Arch. Rubbercultuur* **12,** 7–19(1928). (In English 20–4.)—The report is a summary of tests of the 3 rubbers in comparison with *Hevea* rubber, made from 1916 to 1925, and includes detns. of the ash, N content, acetone ext., viscosity and vulcanizing properties with S alone, with S-hexamethylenetetramine-ZnO and with S-PbO. Rubber

from *Ficus elastica* had a higher acetone ext. and much slower rate of vulcanization than *Hevea* rubber. The plasticity was usually greater also, and the tensile strengths were low. Rubber from *Castilloa elastica* cured more slowly than *Hevea* rubber, had a higher acetone ext. (which was not diminished by previous water extn.) and resembled *Ficus* rubber more than *Hevea*. On the other hand *Manihot glaziovii* (*Ceara*) rubber more nearly resembled *Hevea* in compn. and in its rate of vulcanization. It coagulated spontaneously when dild. with water. It has a very high viscosity, high acetone ext. and low tensile strength when cured. A representative sample of latex contained 21–22% rubber. C. C. DAVIS

Coagulation, structure and plasticity of crude rubber. O. DE VRIES. *Trans. Inst. Rubber Industry* **3**, 284–303(1927).—Expts. in which plasticity and vulcanization tests of rubber contg. varying proportions of serum substances were made show that the serum substances have little or no influence on the plasticity of the resulting rubber but they do tend to decrease the slope of the stress-strain curves of the cured rubber. Therefore the dry serum residues deposited irregularly throughout the rubber do not act as a lubricant but rather increase the internal friction. When rubber prepd. by evapn. of latex films was extd. with water and stored, the plasticity decreased so that the rubber was considerably softer after 1 yr., whereas rubber prepd. similarly but not extd. became harder. Kerbosch rubber and latex-sprayed rubber harden for the same reason. In general, reduction of serum substances (by using dil. latex, by washing or by soaking crepe or sheet in water) gives products which become softer. Therefore to obtain a rubber of invariable plasticity, which is of great importance commercially, the proportion of serum substances must be controlled closely. The content of serum substances best suited for const. plasticity may, however, not conform to that which imparts the best aging properties to the vulcanized rubber, and a systematic study should be made of the influence of the individual serum substances. Besides the serum substances, proteins are pptd. during coagulation and these may form a network in the coagulum. Removal of these from rubber (by centrifuge methods) or increasing their proportion had little influence on the plasticity. Different methods (mech. pressure, EtOH, thymol or coalase) of coalescing the flocculates of heated latex (1:9) had very little influence on the plasticity of the rubber. The expts. indicate that it is difficult to produce by manipulation of the non-rubber components a soft rubber which has a tendency to become tacky or hard. A discussion of closely related earlier work by de V. and others is included, and a general open discussion follows the paper. C. C. DAVIS

Phenomena of swelling. The swelling of rubber. P. STAMBERGER. *Rec. trav. chim.* **47**, 316–28(1928); cf. *C. A.* **21**, 3767; Klein and S., *C. A.* **19**, 1064.—Expts. deal with the extent of swelling of unmilled rubber (I), dead-milled rubber (II) and dead-milled rubber contg. various proportions of C black (III) in solvents and in their vapor. When swollen to the same degree in vapors, the consistency of I, II and III differed greatly. I maintained its structural shape and was very elastic and almost without tackiness, whereas II became a viscous liquid. With III the greater the proportion of C black the greater its structural strength. With 5 vol.-% C black, swelling was still unlimited and the mass lost its form, but with higher proportions of C black the structural form remained as with I. In excess liquid solvent, I and III contg. 20 vol.-% C black maintained their structural form, even though the swelling was unlimited. With III contg. less C black and with II, swelling was unlimited and the structure disappeared. In liquids the magnitude of the swelling differed greatly with I, II and III, whereas in vapor the magnitude of the swelling of I, II and III was the same for a given vapor pressure. This does not mean, however, that mastication fails to cause deep-seated changes, as maintained by Pohle (cf. *C. A.* **15**, 1089). The relative magnitudes of swelling in liquid and in vapor were very different with I compared with II, the swelling of I being around 16 times as great in liquid C_6H_6 as in C_6H_6 vapor, whereas the swelling of II in liquid C_6H_6 was less than twice that in C_6H_6 vapor. The phenomena observed cannot be explained by any concept of swelling suggested up to the present time, and both material and structural factors are probably involved, the former being independent of the swelling medium, the latter being evident only in a liquid (cf. Terzaghi, *Colloid Symposium Monograph* **IV**, 58). C. C. DAVIS

Latex contaminated with copper compounds as a source of danger of fire. J. G. FOL AND W. DE WISSER. *Bull. Rubber Growers' Assoc.* **10**, 124–7(1928).—Double texture cotton fabric rubberized with latex became on standing rolled up so hot that the fabric scorched and the rubber became resinous. Investigation showed that the fabric contained no Cu, but that the latex had been stored in a brass tank and that the NH_3 in the latex dissolved enough Cu to cause the subsequent rapid oxidation. Systematic expts. therefore were carried out with the Mackay app. (cf. Lewkowitsch, *Chem.*

Technology and Analysis of Oils, Fats and Waxes, **III**, 99(1915); *C. A.* **9**, 1852) in which cloth impregnated with (1) pure ammoniated latex, (2) CuO-NH_3 soln. and (3) latex in which Cu had been immersed for 24 hrs. (290 mg. Cu per l. or 40 mg. per sq. m. of fabric) was used. With (1) and (2) there was no rise of temp. above the 92° used as a medium, but with (3) the temp. rose in 45 min. to 249°, which caused complete oxidation and distn. of the rubber and charring of the cotton, and the temp. then returned toward its original value. The expts. show the danger of spontaneous combustion, particularly when rubberized cloth with Cu present is rolled while still warm. Cu or brass equipment must be avoided. C. C. DAVIS

Aldol-α-naphthylamine [as a rubber accelerator]. H. KLOPSTOCK. *Kautschuk* **1928**, 40.—Comments on expts. by Esch (cf. *C. A.* **22**, 511) with aldol-α-naphthylamine. The latter has a slight accelerating action. **Reply.** WERNER ESCH. *Ibid* 40–1. C. C. DAVIS

Adsorption and diffusion of gases through rubber and balloon fabrics. A. DUBOSC. *Rev. gén. caoutchouc* Feb., **1928**, No. 39, 7–8.—A review and discussion of the general phenomena. C. C. DAVIS

Jelutong. C. D. V. GEORGI. *Malayan Agr. J.* **15**, 400–7(1927).—Jelutong may deteriorate by drying to a brittle mass or by becoming sticky and resinous through mold (cf. *C. A.* **22**, 183). In an exptl. study of the *causes of such deterioration*, jelutong latex was coagulated with AcOH, HCO_2H, H_2SO_4, K alum and Na_2SiF_6, let stand 3 days, squeezed and dried slowly with periodic examn. After 7 months only the sample coagulated with Na_2SiF_6 was in good condition, and the moisture in this had decreased from 60 to 15%. Aside from Na_2SiF_6, which prevented mold development, the order of merit of the coagulants was AcOH, HCO_2H, H_2SO_4 and K alum. With K alum the product had become a brown-black sticky mass. In further expts. the same coagulants were used, but the coagula were creped. Deterioration was less rapid, but again the only product which did not deteriorate was that with Na_2SiF_6. Coagulated with EtOH, jelutong dried more rapidly than with the other agents, and after 7 months it contained only 1% water. The results indicate that mold development is the chief cause of deterioration, and since the sugars and gums are attacked, removal of these by boiling jelutong in water greatly retards deterioration. Jelutong, refined by boiling and dried, showed no deterioration from drying or fungoid growth after 14 months, though the moisture was then only 2%. This is confirmed by new reports from America on the good quality of jelutong prepd. by boiling the acidified latex and then boiling the coagulum with water. Though Na_2SiF_6 is shown to be an excellent coagulant, its toxic properties preclude its use. The addn. of soap emulsion when refining the coagulum is unnecessary and does not influence the aging. Jelutong prepd. by boiling acidified latex is less porous and dries more slowly than that prepd. by allowing the acidified latex to stand. C. C. DAVIS

The colloidal and elastic properties of polyvinyl acetate. G. S. WHITBY, J. C. MCNALLY AND W. GALLAY. *Trans. Roy. Soc. Can.* **22**, 27–32(1928).—Polyvinyl acetate (cf. German Patents 271,381, 403,784, 281,687, 281,688; Staudinger, Frey and Starck, *C. A.* **22**, 215) swells and dissolves generally in polar org. liquids, and dissolves in the lower fatty acids, ketones, alcs. and esters, but less readily in the higher members of such homologous series. It also dissolves in liquids of high dielec. const., *e. g.*, AcCN and $MeNO_2$. It is insol. in paraffin hydrocarbons, but resembles hydrocarbon colloids in its soly. in $CHCl_3$ and aromatic hydrocarbons. When heated or swollen in solvents it becomes elastic, and this property is shown when the polymerization is low and corresponds only to a hexamer. Unlike rubber, it fails to give an x-ray fiber diagram when stretched. Unlike sols of most lyophilic colloids, the relative viscosity of its sols changes only slightly with change of temp. Polyvinyl acetate is chem. heterogeneous, and a representative sample prepd. with benzoyl peroxide contained mols. with mol. wts. from 566 to 6192. There is an approx. linear relation between the state of polymerization and the viscosity of C_6H_6 sols. A study of the swelling or solvent power of various hydrocarbons, esters, ketones, alcs., ethers, acids, aldehydes, halogenated hydrocarbons and certain other representative compds. showed that the best solvents are HCO_2Me, HCO_2Et, AcCN, Me_2CO, $CHCl_3$, AcH, $CH_2(OMe)_2$ and $MeNO_2$, the power of the solvents decreasing in the order cited. C. C. D.

Some derivatives of β,γ-dimethylbutadiene. A. D. MACALLUM AND G. S. WHITBY. *Trans. Roy. Soc. Can.* **22**, 33–8(1928).—Modifying a method already described (German Patent 233,894), 42% of pinacone hydrate (I) was obtained from Me_2CO. Fused over NaOH, I was converted to pinacone. A comparison of different methods for converting pinacone to β,γ-dimethylbutadiene (II) showed the best results by distn. over 10% of K alum (cf. German Patent 250,086). This gave 60% **II**, 22% higher fraction (chiefly pinacoline) and 5% **I**. Sulfanilic acid also gave a good yield. S_2Cl_2

in CS_2 added dropwise to **II** in CS_2, let stand several days in darkness and evapd. *in vacuo* at 50°, yielded an *oil* which on attempted distn. gave a solid *polymer* or *decompn. product*, probably $C_{12}H_{20}Cl_2S_2$, n_D^{26} 1.5400, d_3^{26} 1.1172. With S, **II** in C_6H_6 at 100° gave no thiophene deriv., nor did it react in MeOH at room temp. with $SbCl_3$. Brominated at 0° in CCl_4, Et_2O or EtCl, washed with MeOH, and recrystd. repeatedly, **II** yielded the solid dibromide, $BrCH_2CMe:CMeCH_2Br$ (**III**) (cf. *J. prakt. Chem.* **62**, 166(1900)), $b_{18.5}$ 105–10°, d_4^{50} 1.6912, n_D^{50} 1.5470. The liquid dibromide (**IV**), $b_{18.5}$ 105–10°, n_D^{50} 1.5390, d_4^{50} 1.6502. Ozonization of **III** in very cold EtCl gave 84.15% bromoacetone. **III** heated at 100° with EtONa (calcd. quantity), dild., salted out with KOH, dried and distd., yielded *1,4-dimethoxy-2,3-dimethyl-2-butene*, oil, peppermint odor, $b_{33.5}$ 81–4°. Prepd. similarly, *1,4-diethoxy-2,3-dimethyl-2-butene*, oil, faint rose odor, b_{25} 90–5°. **III** in Et_2O added slowly to excess MeMgI soln., ice and then $HNEt_2$ added, dild. with mineral acid, dried and the Et_2O ext. distd., gave a *terpene oil*, $C_{12}H_{20}$, b_{20} 50°, not the normal terpene of Lebedev and Merezhkovskii (*C. A.* **8**, 320) and a residue with high b. p. **III** in C_6H_6 heated 4 hrs. at 100° with $HNMe_2$ (2 mols.), extd. with dil. HCl, the acid ext. extd. with Et_2O, made alk., again extd. with Et_2O, the aq. soln. made acid to Congo red and H_2PtCl_6 added, yielded *1,1,3,4-tetramethyl-Δ^3-pyrrolinium bromide platinichloride* $C_{16}H_{32}N_2Cl_6Pt$, yellow, m. 199°. A higher yield was obtained by pptn. as the *auribromide*, red. Washed with water, extd. with dil. HCl and made acid to Congo red, and pptd. with a Au salt, the combined Et_2O exts. pptd. 23.4% of *1,4-bisdimethylamino-2,3-dimethyl-Δ^2-butene dihydrobromide aurichloride*, $(BrHMe_2NCH_2CMe:)_2Au_2Cl_8$, yellow, m. 188–9°. The tendency toward ring formation is therefore less in **III** than in the solid dibromide of Braun (*C. A.* **17**, 1083–4). Following the same procedure was prepd. after purification from EtOH, *1,4-diphenylmethylamino-2,3-dimethyl-Δ^2-butene*, $(PhMeNCH_2CMe:)_2$, m. 76–7°. The aq. soln. gave no ppt. with Au or Pt chlorides or picric acid. From **III** and C_5H_5N (20 parts) was obtained, after purification from Et_2O, *2,3-dimethyl-Δ^2-butene-1,4-dipyridonium dibromide*, $(PhBrNCH_2CMe:)_2$, m. 124°. *Platinichloride*, $C_{16}H_{20}N_2Cl_6Pt$, m. 229° (decompn.). **IV**, $HNEt_2$ (2 mols.) and Et_2O (50 parts) let stand 1.5 days, evapd. and the products isolated in the way described for the auribromides yielded 26.75% *quaternary salt*, $C_{10}H_{20}NBr_4Au$, dark red, m. 106–7°, and 21.22% of *ditertiary salt*, $C_{14}H_{32}N_2Br_8Au_2$ (**V**), orange, purified by pptn. with Et_2O from MeOH, m. 177–8°. By the same method **III** gave 11.55% of *quaternary salt* (28.78% Au), m. 52.8° and 27.2% of *ditertiary salt*, m. 177–9° (unchanged by mixing with **V**). The greater tendency of **IV** to form a ring compd. showed that it is the *cis*-form and **III** the *trans*-form. Other reasons are given to show that **IV** is the *cis*-form. Since, however, the quaternary compds. from **III** and **IV** were not identical, **IV** as prepd. may have been a mixt. or the product from **III** may have been bimol., thus: $BrEt_2NCH_2CMe:CMeCH_2N(Et_2Br)CH_2CMe:CMeCH_2$, instead of $MeC:CMeCH_2N(Et_2Br)CH_2$. **III** refluxed with Zn dust and 90% EtOH, extd. with Et_2O and the ext. brominated yielded **III**. **III** in dry Et_2O with Mg ($^1/_2$ atom) gave no trace of *rubber* or $C_{12}H_{20}Br_2$, but only **IV**. **III** heated 12 hrs. at 100° with **II** gave **II**, **III** and **IV**.

C. C. DAVIS

A new tetramethylbutadiene. A. D. MACALLUM AND G. S. WHITBY. *Trans. Roy. Soc. Can.* **22**, 39–44(1928).—The expts. are part of a study of the influence of methylation on the ability of butadiene to polymerize, earlier work having indicated that methylation of the end positions has, compared with methylation of the middle positions, an unfavorable effect, and that the greater the no. of Me groups the less the tendency to polymerize. *Reduction of MeEtCO to 3,4-dimethylhexan-3,4-diol* (**I**) was tried under various conditions. Na and moist Et_2O gave a 9.5% yield. In C_6H_6, Fe or Zn gave no yield, Al and Mg gave a 40% yield (Mg acting much more rapidly), amalgams were not better than the corresponding metal with $HgCl_2$, small proportions of I or CuCl did not increase the yield, too great diln. with C_6H_6 diminished the yield and excess ketone ruined the yield. The best crude yield (41%) was obtained by refluxing Mg shavings (1 equiv.) with $HgCl_2$ (0.0747 mol.), MeEtCO (2.22 mols.) and C_6H_6 (2.13 mols.), adding when stiff more C_6H_6 (1.06 mol.), decompg. with ice, adding NaOH (2 mols.), drying over NaOH, distg. *in vacuo* and purifying by fractionation. **I** (10–30 g.) and 20% H_2SO_4 (1 drop) distd. at 140–50°, the oil sepd., dried over $CaCl_2$, fractionated *in vacuo*, gave 84% of crude product which on further fractionation under 100 mm. pressure gave *3,4-dimethylhexa-3,4-diene* (**II**), b. 132–4°, b_{100} 71–3°, n_D^{25} 1.4630, $d_4^{19.2}$ 0.7832, $[\alpha]$ 38.78. In soln. with Br at 0° it absorbs 2 atoms of Br, and on standing at 20° it absorbs 4 atoms with evolution of HBr, yielding

a *dibromide*, could not be crystd. and decompd. on standing at 20°. Excess 3% aq. $KMnO_4$ added to **II**, filtered, neutralized with HNO_3, excess $AgNO_3$ added and evapd. *in vacuo* yielded AcOAg. Crude **II** may contain a structural isomer, for fractions above and below its b. p. had the same compn. but different *n* values and oxidation yielded a *Ag salt* contg. less Ag. **II** did not undergo thermopolymerization when heated at 100° under 28 mm. pressure. Neither was it polymerized by long standing with Na. Dissolved in concd. H_2SO_4 and pptd. with water, **II** formed a viscous liquid *compd.*, b. 170–200°, n_D^{25} 1.4915, contg. 85.4% C and 12.69% H and probably an impure dimer. Unlike isoprene and dimethylbutadiene, it does not react with aq. SO_2. Exposed to air **II** undergoes autoxidation, forming a gummy *polymer*. Short exposure to a deficiency of air formed a colorless *gum*, which purified with MeOH contained 67.1% C and 10.01% H, gave a strong peroxide reaction with hot titanic acid, but a negative test with KI. **II** probably differs from a compd. of the same compn. prepd. by Herschmann (*Monatshefte* **14**, 233(1893)). Attempts to brominate *n*-BuBr by prolonged exposure to light with Br and water gave negative results. With the Linnemann method (*Ann.* **161**, 199(1872)) 15.5% of a *dibromo compd.*, b. 170–80°, was obtained, probably a 1,3-1,2-deriv. Reboul's method (*Bull. soc. chim.* **7**, 124(1892)) and Fe as catalyst gave 32.6% of the 2,3-dibromide (*Ann.* **144**, 234). Therefore Fe causes isomerization during bromination. In prepg. MeCH:CMeBr, it was found best to use excess KOH (cf. *Ann.* **253**, 231(1889)), 263 g. of dibromide, 82 g. of KOH and 400 cc. of MeOH, giving 124.7 g. of MeCH:CMeBr, b. 89–93°. Treated in dry Et_2O with Mg and with I as catalyst, decompd. with ice and dil. AcOH and distd. it gave, not the diene desired, but the *compd.* $C_{16}H_{34}O$, oil, onion odor, boiling approx. 160°, n_D^{25} 1.4735. The compn. of **II**, as indicated by the formation of AcOH on oxidation, is MeCH:CMeCMe:CHMe. C. C. DAVIS

Comparative study of the addition of zinc oxide, lithopone, zinc sulfide and titanic acid to thin-walled rubber products vulcanized with sulfur chloride. RUDOLF DITMAR AND GUSTAV BALLOG. *Gummi-Ztg.* **42**, 1303–4(1928).—Expts. indicate that 8% is about as much "colloidal" pigment as can be added to rubber cured with S_2Cl_2 vapor or S_2Cl_2 in CS_2 without causing imperfect goods. Using this max. of 8%, the relative merits of ZnO, ZnS, lithopone and TiO_2 were detd. ZnO imparted the most nearly white color; in all cases the quality was good when new and there was no essential difference in the aging. C. C. DAVIS

Direct determination of rubber in soft vulcanized rubber. A. R. KEMP, W. S. BISHOP AND T. J. LACKNER. *Ind. Eng. Chem.* **20**, 427–9(1928).—When somewhat modified, the Wijs method, which has already been shown to be suitable for raw rubber (cf. *C. A.* **21**, 1901), is applicable to the detn. of the rubber content of vulcanized rubber. Ext. the sample with Me_2CO, then with $CHCl_3$, ext. with alc. KOH if factice is present, disperse the dry residue (0.07–0.10 g.) in $(CHCl_2)_2$ (50 cc.) by refluxing, dil. with pure CS_2 (25 cc.), add 0.02*N* Wijs soln. (25 cc.), keep cold for 2 hrs., add 15% aq. KI (25 cc.) and water (50 cc.), titrate with 0.1 *N* $Na_2S_2O_3$, adding 5% starch soln. (5 cc.). From the difference between the blank and sample titration is calcd. the I no. as before (*C. A.* **21**, 1901). To det. combined S, disperse the extd. residue (0.5 g.) in $(CHCl_2)_2$ (50 cc.), make up at 25° to 250 cc. with CCl_4, centrifuge or let settle, evap. 100 cc. to dryness and det. S by the method of Waters and Tuttle (Bur. Standards, *Sci. Paper* **174**(1911); cf. *C. A.* **6**, 1540). From the sum of the hydrocarbons in the unsatd. and combined states is calcd. the total rubber content. The various factors influencing the precision are discussed and representative analyses are given. Factice is about the only org. or inorg. ingredient which ordinarily affects the results. $(CHCl_2)_2$ was chosen as the best of numerous solvents of vulcanized rubber. C. C. DAVIS

The effect of mineral rubber on the tensile strength of vulcanized rubber. WERNER ESCH. *Kautschuk* **1928**, 31–5.—Papers by Stoll (*C. A.* **22**, 888) and by Ditmar (*C. A.* **22**, 1061) on the properties and effects of "mineral rubber" are reviewed critically. Phys. tests of several vulcanized mixts. are tabulated to show that the effect of "mineral rubber" depends upon the temp. and time of vulcanization, on the particular accelerator and its proportion and on the proportion of S. The addn. of small proportions, *e. g.*, 5%, tends to stiffen a vulcanized mixt. and also to accelerate its rate of vulcanization. C. C. DAVIS

Measurement of resistance of vulcanized rubber to penetration of benzene and other combustible substances. F. C. SCHMELKES. *Ind. Eng. Chem.* **20**, 430–1(1928).—The method is particularly suitable for hose. A definite length and diam., *i. e.*, a const. surface of the latter, is surrounded by the solvent (C_6H_6, gasoline, etc.) and air is blown through the hose at a definite and const. rate. The issuing air is then analyzed continuously for its solvent content by a *calorimetric device operating a current recorder*. Besides the dimension of the hose, such factors as temp. must be controlled. C. C. D.

The resistance to stretching of vulcanized rubber. II. R. ARIANO. *Nuovo cimento* [N. S.] **4,** 263–81(1927).—A. has extended his investigations (*C. A.* **20,** 3362) to a consideration of the effect of various inorg. ingredients, to a study of the variation in vol. with respect to the Joule effect and to an examn. of the degree of vulcanization upon the parameters characteristic of stretching. He had demonstrated the independence of the type of mixt. and of the degree of vulcanization (Poisson's coeff.) and explains various characteristic parameters and their phys. significance. L. T. F.

Hard rubber for the chemical industry. J. R. SILVER. *Trans. Am. Inst. Chem. Eng.* **19,** 71–7(1927).—A review of the properties and uses of hard rubber. C. C. D.

Rubber in engineering. J. W. SCHADE. *Trans. Am. Inst. Chem. Eng.* **19,** 57–70 (1927).—A review of the useful properties of rubber and its present wide field of application. C. C. DAVIS

Rubber inventions and processes. ANON. *Bull. Rubber Growers' Assoc.* **10,** 183–4(1928).—Eight British and German patents are described. C. C. DAVIS

Development of the present automobile tire. W. F. ZIMMERLI. *Trans. Am. Inst. Chem. Eng.* **19,** 79–92(1927).—Descriptive. C. C. DAVIS

The industrial application of rubber latex. PHILIP SCHIDROWITZ. *Trans. Inst. Rubber Industry* **3,** 362–80(1928).—A crit. review of present developments, including the concn., preservation, handling, transport and variability of latex, and its use in tires, casings, inner tubes, proofed goods and dipped goods. A general discussion follows the paper. C. C. DAVIS

The testing of rubber goods for sunlight effect. H. E. WEIGHTMAN. *Rubber Age* (N. Y.) **23,** 75–6(1928).—Exposure of vulcanized rubber mixts. to ultra-violet light showed effects which differed from the effects of sunlight, particularly with mixts. contg. reclaimed rubber, in the latter case mixts. which failed in service being comparatively resistant to ultra-violet light, and *vice versa*. The use of a violet C arc gave results conforming more closely with those for exposure to sunlight. An *app. for duplicating the effect of sunlight and air* is described, in which the temp., humidity and air supply are controlled while the rubber under tension is exposed to artificial light of known wave lengths which resemble sunlight in their relative intensities. C. C. DAVIS

Remarks on plasticity determinations in the Williams press. O. DE VRIES. *India Rubber J.* **75,** 429–30(1928).—In comparative tests of different types of unmasticated rubber in the ordinary Williams plastometer and in the modified form of de Visser (cf. *C. A.* **20,** 839) in which a const. pressure per unit surface is exerted on the rubber, the de Visser method gave irregular results which bore no relation to the corresponding results with the original Williams method. These irregular results with the de Visser app. were proved to be due to inherent mech. difficulties and it is considered that until this general method of detg. plasticity is placed on a mathematical basis, the de Visser app. is less reliable than the original Williams app. C. C. DAVIS

The distribution of fillers in rubber mixtures. ST. REINER. *Gummi-Ztg.* **42,** 1359–60(1928).—Detns. of free S and of the ash at different points in representative rubber mixts. prepd. under ordinary factory conditions showed unexpected variations. Thus the ash of a mixt. which had not been calendered was 53.95–63.60%, a variation which was greatly reduced after calendering. Mixts. prepd. in the wet way showed relatively little variation. C. C. DAVIS

The relation between the cotton and rubber industries. R. TRUESDALE. *Trans. Inst. Rubber Industry* **3,** 269–85(1928).—A crit review and discussion of the use of cotton in the rubber industry, with data showing the structure and phys. properties of different cotton cords and fabrics. C. C. DAVIS

Guanidine accelerators. History and litigation. ANON. *Rubber Age* (N. Y.) **23,** 79–80(1928). C. C. DAVIS

The application of the analytical quartz lamp in the rubber laboratory. F. KIRCHHOF. *Kautschuk* **1928,** 24–7.—A study similar to that of Nagle (cf. *C. A.* **22,** 1251) was made of various inorg. and org. rubber ingredients or substances of interest in rubber manuf. to det. how many of them can be identified by means of characteristic *fluorescent colors* when viewed in ultra-violet light. The light was filtered so that the samples were lighted only with radiation of 3000–4000 A. U. The characteristic fluorescence of substances depends upon their purity, and the presence of impurities greatly changes these fluorescent colors. Thus com. ZnO varies considerably because of differences in impurities (cf. Nagle, *loc. cit.*), varying from S-yellow for the purest grade to dark yellow-ocher, greenish yellow or pale rose. Since $BaSO_4$ is a brown-violet and ZnS a bright orange, the fluorescence of lithopone varies with the ZnS content. Many other inorg. compounding ingredients give characteristic colors which in most cases differ greatly from their colors in sunlight. Among aliphatic substances, vegetable and animal oils, fats and waxes and paraffin hydrocarbons show characteristic fluorescent colors. Phenols

and aromatic acids show particularly bright colors and with increase in complexity of the ring, *e. g.*, quinoid compds., the intensity of the fluorescence becomes particularly great. On the other hand, NO_2 groups weaken the fluorescence. The introduction of Zn into feebly fluorescent compds. increases greatly the fluorescence, *e. g.*, quinosol, which is not fluorescent, becomes strongly so when converted to its Zn deriv. Dyes, org. rubber accelerators and antioxidants are also among the groups in which many of the individual members show characteristic colors. Proteins, sugars, starch and resins show more or less strong fluorescence. Different types of rubber show different fluorescent colors and when compounding ingredients are added these colors change so that sometimes it is possible to det. qualitatively the nature of a mixt. The differences in color of the various rubbers depend chiefly upon the acetone ext. and the exts. of different rubbers show different colors. In general, ultra-violet light analysis is useful in rubber technology for *identifying ingredients, controlling their purity* and *judging the correctness or thoroughness of a mixing.* It should also be of value in following the *natural or artificial aging of rubber mixts.* through oxidation. C. C. DAVIS

The identification of dusting agents on thin-walled rubber articles, cured with sulfur chloride, by means of the Hanau analytical quartz lamp. RUDOLF DITMAR AND WILHELM DIETSCH. *Gummi-Ztg.* **42,** 1415(1928).—Different types of dusting agents, *e. g.*, starches, talc, $CaCO_3$, etc., can be readily identified by examg. them in filtered ultra-violet light (cf. preceding abstr.), under which conditions they show characteristic fluorescent colors. Even starches from different sources can be distinguished. Org. accelerators also show characteristic colors which allow their identification.

C. C. DAVIS

Patents

Preserving latex. A. E. JURY and O. H. SMITH. Brit. 268,219, June 8, 1926. See U. S. 1,619,938 (*C. A.* **21,** 1378).

Treating latex. J. MCGAVACK. Brit. 268,299, March 24, 1926. See U. S. 1,647,805 (*C. A.* **21,** 333).

Rubber articles from latex. E. HOPKINSON and W. A. GIBBONS. U. S. reissues 16, 873–4, Feb. 7. See original pat. 1,542,388 (*C. A.* **19,** 2425).

Apparatus for rubberizing fabrics. W. W. BENNER and E. A. HOENER. U. S. 1,658,366, Feb. 7.

Procedure for making rubber shoes, etc., from pre-vulcanized aqueous rubber dispersions. W. B. WIEGAND and P. SHIDROWITZ. Brit. 267,186, Nov. 10, 1925.

Fixing hairs, fibers, etc., for brushes, artificial furs, etc., by use of rubber. BRITISH DYESTUFFS CORPORATION, C. J. T. CRONSHAW and W. J. S. NAUNTON. Brit. 267,404, Oct. 15, 1926. A rubber compn. is used which is vulcanized at a low temp. by a "super-accelerator" such as Zn alkylxanthate.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 267,808, Sept. 3, 1926. A porous adsorbent such as powd. activated C is used for removing liquid polymerization products from synthetic rubber.

Rubber compositions for tires or other articles. R. GRIMOIN-SANSON and H. DANEL. Brit. 268,280, March 26, 1926. Rubber 20, cork 2.5 and emery 3 parts are used with vulcanizing agents, accelerators or other auxiliary substances for molded articles.

Apparatus for vulcanizing tire tubes or other rubber articles. A. J. FLEITER, H. C. BOSTWICK and T. A. MILLER. U. S. 1,658,376, Feb. 7.

Procedure and apparatus for spray desiccation of rubber latex, etc. E. HOPKINSON. Brit. 269,157, April 10, 1926.

Electrodeposition of rubber. S. E. SHEPPARD and C. L. BEAL. Brit. 268,717, April 1, 1926. Fabrics on which rubber is to be deposited are preliminarily impregnated with a size preferably comprising a hydrophilous colloid such as glue, starch or dextrin acidified with HOAc, formic acid, oxalic acid, lactic acid or other acid to a p_H between 3 and 7. The sizes may also contain acid salts, highly ionized neutral salts or alc. Various details are given, and an app. is described.

Electrophoretic deposition of rubber. ANODE RUBBER CO., LTD. Brit. 269,504, April 15, 1926. Porous molds used in electrophoretic deposition of rubber from latex are heated, after use, to reverse changes they have undergone during the deposition. A current may be passed through them in reverse direction to that used for the deposition or the molds may be rinsed with an alk. soln. such as NH_3. With inert molds, an electrolyte contg. a Ca salt, with or without a Mg salt, may be used for impregnating the mold. Brit. 269,505 specifies electrophoretic deposition of rubber while preventing liberation of gas at the cathode, *e. g.*, by an oxidizing depolarizing agent such as PbO_2. An app. is described.

Treating metal molds for molding rubber. J. D. COMSTOCK. U. S. 1,662,365, March 13. The mold surfaces are treated with a caustic cleaning soln. and rubbed to remove dry foreign matter, sprayed with a thin soln. of enamel or varnish such as "spar varnish" and baked to harden the enamel, cooled, treated with a second coat of enamel and baked again.

Regenerating rubber. C. DANIER. Brit. 269,127, April 8, 1926. Waste rubber (such as tire treads or like articles) is distd. to yield an oil consisting largely of isoprene and heveene. Other waste, such as cut up tire covers, is impregnated with this oil and plunged into concd. HCl to polymerize the hydrocarbons and destroy the fabric insertions. After 15–20 days, the viscous mass is washed and passed through a crepe machine to remove the destroyed canvas or the like and leave a product suitable for general uses similar to those of "plantation rubber" except for making solns. Cf. *C. A.* **22,** 1061.

Preserving rubber. C. R. BOGGS and J. T. BLAKE. Brit. 269,124, April 6, 1926. Rubber-contg. bodies of elastic character such as elec. insulations are made resistant to ozone by coating them with a plastic layer such as a compn. formed from balata or chicle 35, reclaimed rubber 5 and "vegetable or animal oil substitute" 60 parts. The compn. may be vulcanized short of becoming resilient.

Preserving rubber. S. M. CADWELL. U. S. 1,662,182, March 13. Deterioration of rubber is retarded by use with it of an excess of a condensation product such as formed from $PhNH_2$ and AcH which serves both as an accelerator in soft vulcanizing and as a retarder of deterioration.

Preserving rubber. B. D. PORRITT, T. R. DAWSON AND RESEARCH ASSOCIATION OF BRITISH RUBBER & TYRE MANUFACTURERS. Brit. 269,745, May 25, 1926. Deterioration of rubber goods by the action of light and air is restricted by the use in the rubber compn. of small proportions of antioxidants such as dyes or coumarin compds.

Rubber compositions. F. C. DYCHE-TEAGUE. Brit. 268,853, Dec. 10, 1925. A vulcanizable compn. is prepd. by mixing rubber with finely divided C deposited on a catalyst as described in Brit. 160,561 (*C. A.* **15,** 2342). Preferably, the catalyst used comprises equal quantities of Fe and Ni formed by reduction of their oxides by CO at 500° and a suitable mixt. comprises rubber 200, C black contg. 5–10% of the catalyst 72, ZnO 20, S 8 and diphenylguanidine 2 parts.

Coloring aqueous dispersions of rubber. M. C. TEAGUE. U. S. 1,660,213, Feb. 21. See Can. 270,530 (*C. A.* **21,** 3489).

Binding agent for use in coloring compositions, varnishes and cements. J. TENGLER. U. S. 1,660,851, Feb. 28. Pulverized old rubber is heated under pressure with hydronaphthalene which effects formation of H_2S and $C_{10}H_8$; the rubber is then dissolved in a solvent such as C_6H_6, having a lower b. p. than $C_{10}H_8$; the $C_{10}H_8$ is removed, *e. g.*, by cooling to cause sepn., and the rubber is revulcanized in the presence of the solvent.

Hollow metallic forms for marking rubber gloves or similar articles. E. WHITE and J. MCCARTHY. Brit. 269,223, Aug. 24, 1926.

Joining layers of rubber with each other or with other materials. F. J. DAVIS. Brit. 269,224, Dec. 15, 1925. See U. S. 1,654,240 (*C. A.* **22,** 889).

Paving composition comprising rubber. E. HOPKINSON. U. S. 1,661,828, March 6. A surfacing material is prepd. by mixing different batches of aq. rubber compns. such as latex mixts. with ingredients which are effective together but not separately as vulcanizing agents; H_2O is then removed from the compns. and they are mixed and vulcanization is effected *in situ* on a paving foundation.

Vulcanizing rubber articles. C. DRESSLER. U. S. 1,662,804, March 13. The articles are moved through a chamber in which they are heated to effect vulcanization; a cooling medium such as air, CO_2 or H_2O is injected into the chamber when necessary to prevent overheating of the articles. An app. is described.

Continuously vulcanizing rubber stock. G. F. FISHER. U. S. 1,661,888, March 6. The stock, which may be in the form of tubing, is carried in molten metal, glycerol or other moving liquid stream through a vulcanizing chamber and heat is supplied to the carrying liquid. An app. is described.

Rubber vulcanization accelerator produced by action of formaldehyde on the product of aniline and acetaldehyde. C. O. NORTH. U. S. 1,659,151, Feb. 14. See Brit. 251,005 (*C. A.* **21,** 1378).

Acetaldehyde and rubber vulcanization accelerators. C. N. HAND. Brit. 269,556, April 12, 1926. AcH mixed with C_2H_2, such as is obtained by the reaction of C_2H_2 with H_2SO_4 in the presence of a catalyst, is passed through a material with which the AcH will combine, *e. g.*, a primary amine, and the reaction is allowed to proceed until combination of 3 mol. proportions of aldehyde to 2 mol. proportions of the amine is

effected. Aminophenol or *p*-aminodimethylaniline may be used and a vulcanization accelerator is thus produced.

Preserving vulcanized rubber. H. W. FIEDLER. U. S. 1,661,887, March 6. A paste for preserving vulcanized rubber is prepd. by mixing glycerol, BzH and talcum, introducing the mixt. into a soln. of raw rubber in paraffin oil at a temp. of about 140° and then raising the temp. to about 180°.

Vulcanite. H. P. STEVENS. Brit. 269,693, Jan. 28, 1926. A mixt. of rubber (other than latex) is heated at a comparatively low temp. (suitably about 100° for 24 hrs.) with a high proportion of S and a powerful accelerator. The mixt. may comprise rubber 100, S 75, ZnO 20 and Zn diethyl dithiocarbamate 5 parts. Zn propyl xanthate also is a suitable accelerator.

Preserving latex. I. G. FARBENIND. A.-G. Brit. 271,863, May 28, 1926. Latex is protected against premature coagulation by addn. of a H_2O-sol. deriv. of NH_3 such as a mono-, di- or tri-alkylamine, cyclohexylamine, benzylamine, piperidine and its alkyl derivs. or trihydroxyethylamine.

Jelutong latex. S. S. YATES. Brit. 271,329, June 19, 1926. Jelutong latex is coagulated and then dried until the product contains less than 5% moisture. The coagulated product may be sheeted or creped before drying.

Apparatus for working rubber. R. C. LEWIS. Brit. 271,070, May 17, 1926.

Machine for mixing rubber. R. C. LEWIS. Brit. 271,075, May 17, 1926.

Rubber compositions. W. B. WESCOTT. Brit. 272,187, June 1, 1926. Fibrous material such as tire or belt scrap, cotton batting, ramie or animal or mineral fiber is impregnated with latex, dried or treated with a coagulant and milled. The product may be used for shoe soles, belting, hose, rolls or other products. Various details are given.

Coating composition containing rubber. C. M. STINE. U. S. 1,663,100, March 20. In prepg. a compn. suitable for coating metal, wood, cloth, leather, paper, etc., unvulcanized rubber 10 is dissolved in a rubber solvent such as C_6H_6 with 4–31 parts of a drying oil such as linseed oil and with a quantity of drier equal to 0.4–5.0% of the oil and the mixt. is heated in the form of a thin film to 70–125° to volatilize the solvent, oxidize the oil and cure the rubber. U. S. 1,663,101 relates to generally similar compns.

Coating composition containing rubber. C. COOLIDGE and H. E. EASTLACK. U. S. 1,663,119, March 20. Rubber is dissolved in C_6H_6 or other suitable solvent, assocd. with a pigment such as Prussian blue or C black, which ordinarily gives rise to "lobbering" and a small proportion (suitably 0.05–10%) of oleic acid or similar substance is used as a "delobbering agent."

Composition for use on heated surfaces used in shaping rubber. J. M. CRANZ. U. S. 1,662,958, March 20. A sugar such as sucrose or molasses is mixed with Na hyposulfite or other alkali metal hyposulfite, for use as a coating on mold or press-plate surfaces to prevent adhesion.

Coloring rubber. E. R. BRIDGWATER. U. S. 1,663,436, March 20. Rubber or like material is treated with a vulcanizing agent such as S and with the Na salt of the azo compd. obtainable by coupling diazotized 2-chloro-5-toluidine-4-sulfonic acid with β-naphthol.

Treating differently colored batches of rubber to produce strips with grained surfaces. T. J. MELL. U. S. 1,663,275, March 20.

Porous rubber articles. H. BECKMANN. Brit. 270,374, Jan. 27, 1926. Rubber with very small pores suitable for use in making moistening pads or rollers for printing machines or in lubricating pads or "wicks" for bearings is obtained by adding $MgSO_4$ soln. to latex with H_2O and S to form a jelly and then vulcanizing this under pressure with H_2O or satd. steam.

Rubber-treated fabric for use as a "buffing-leather" substitute. R. B. RESPESS. U. S. 1,663,954, March 27. A bat formed of separable layers of unspun fibers is impregnated with adhesive, dried and pressed under tension, coated on one side with rubber soln., the coating is vulcanized, and the coated side of the bat is then split from the other side to leave the vulcanized coating with only a thin layer of fibers adhering to one side of it.

"Stuffing" from old rubber tires and scrap. G. J. MILLER. U. S. 1,663,852, March 27. The material is soaked in kerosene to soften it, ground, further treated with kerosene at a temp. not over 200° for a time of from a few min. to several hrs. until the rubber is permanently softened to the desired degree and the mass is then sepd. from the oil and dried.

Regenerating rubber. W. SCHEITHAUER. Brit. 270,675, May 8, 1926. Comminuted scrap rubber is treated with a hot NaOH soln. which has been in contact with cellulose such as wood, sawdust, lignocellulose or cotton, *e. g.*, waste lyes produced in

the manuf. of viscose. The material may be heated under a pressure of 12 atm. for 4 hrs.

Devulcanizing rubber. J. TENGLER. Brit. 271,073, May 11, 1926. Pulverized old rubber is heated under pressure with hydrogenated hydrocarbons such as hydronaphthalene to remove S as H_2S. A solvent such as gasoline or C_6H_6 is added and soln. is effected by the use of heat and pressure. The $C_{10}H_8$ may be removed by cooling. The product may be revulcanized with S for use in paints, varnishes, cements, etc.

Molding and vulcanizing shoe soles or other rubber articles. E. W. DUNBAR. U. S. 1,663,587, March 27.

Vulcanizing rubber. SILESIA VEREIN CHEMISCHER FABRIKEN. Brit. 270,644, May 4, 1926. Ditolylguanidine thiosulfite or other salts of aliphatic or aromatic amines are used as accelerators. Salts of inorg. acids such as sulfates, chlorides, nitrites, sulfites or thiosulfites are preferred.

Vulcanized oils. F. KAYE. Brit. 271,553, Feb. 23, 1926. Emulsified oils or fats, *e. g.*, linseed oil emulsified with alkali, are treated with a sulfide or polysulfide such as that of NH_4, Na, K, Ca or Ba, which results in the formation of a gel, and a coagulant such as $Al_2(SO_4)_3$ may be added which produces quicker drying of the gel. The latter may be mixed with fibers or fillers or may be dried in sheet form or spread on or between sheets of textile material or paper. When used in paper-making, the emulsified oil, together with latex, may be added to the pulp in the beater, with subsequent addn. of alum, $MgSO_4$ or H_2SO_4. Na or Ca phosphates may be added as accelerators.

Latex-coagulating tanks (with linings and partitions of aluminum or other suitable metal). SARCO ENGINEERING & TRADING CO., LTD. Brit. 272,608, March 17, 1926.

Molding rubber articles. A. T. GUSTAFSON. U. S. 1,665,355, April 10. A ready-made foil of cellulose nitrate or acetate compn. or other cellulose derivs. is interposed between the material and the mold surfaces in molding rubber or other materials which are plastic when heated.

Sponge rubber. FEATHERBEDGE RUBBER CO. Brit. 273,223, April 11, 1927. Long lengths of sponge rubber are formed by enclosing a suitable compn. in a fabric tube or the like adapted to allow the compn. to expand during vulcanization. Vulcanization may be effected in a steam chamber and the compn. may be coated with soapstone or the like if it is desired to remove the fabric. Vulcanization also may be effected by drawing the material and covering through a heated metal tube.

Utilizing waste rubber. S. A. OGDEN. Brit. 273,169, Dec. 11, 1926. Waste rubber contg. cellulose such as old tires or shoes is devulcanized and a rubber-cellulose product is obtained by plasticizing the rubber in the presence of an alk. substance such as NaOH and then submitting the mass to a cellulose hydrating treatment, *e. g.*, with H_2SO_4. After washing and neutralization a gelatinous product is obtained having a lower m. p. and greater tensile strength than rubber.

Rubber paving and flooring blocks. C. D. ROTCH and A. I. G. WARREN. Brit. 272,327, May 10, 1926. The under surface of rubber blocks are metallized by a method such as that described in Brit. 196,063 (*C. A.* **17**, 3809) to facilitate securing the blocks to a cement foundation or the like. Finely divided Ag, Ag salts, Zn or Fe may be used and converted by the S used in vulcanizing into a sulfide which penetrates the superficial portion of the rubber and the sulfide deposit may then be reduced and addnl. metal electrolytically deposited.

Zinc oxide for use with rubber. F. G. BREYER, E. H. BUNCE and J. H. WEIKEL. U. S. 1,664,767, April 3. See Brit. 253,875 (*C. A.* **21**, 2538).

Rubber-vulcanization accelerator. C. O. NORTH and W. SCOTT. U. S. 1,664,481. April 3. H_2S is caused to react upon the NH_3 addn. product of a straight-chain aldehyde such as butyraldehyde NH_3 to form an accelerator for vulcanizing with S.

Vulcanizing rubber. CHEMISCHE FABRIK KALK GES. AND H. OEHME. Brit. 272,860, June 21, 1926. ZnO is obtained for use in vulcanization, by decompn., at a relatively low temp., of pptd. $Zn(OH)_2$ or a salt such as the acetate, formate or basic carbonate.

Vulcanizing rubber tubes. L. A. LAURSEN. U. S. 1,665,308, April 10. Tubes to be vulcanized are placed on poles or mandrels, the open ends of the tubes are sealed to the mandrels and the tubes are vulcanized while on the mandrels and in the absence of external confining means solely by direct contact with water or a similar liquid heated to the temp. required for vulcanization. U. S. 1,665,309 specifies placing rubber tubes or other uncured rubber articles on a core, softening the uncured rubber by heat less than that required to cure it, submerging in a liquid such as water at a temp. too low for vulcanization and subjecting to pressure to expel air and prevent its forming blemishes, and then vulcanizing at appropriate temp. U. S. 1,665,310 specifies placing tubes or other rubber articles in a receptacle into which steam is then admitted, and, after

the articles are softened by the steam, admitting water or other suitable liquid to submerge the articles and heating to effect vulcanization. U. S. 1,665,311 specifies spraying the water on the articles before heating to effect vulcanization. U. S. 1,665,312 specifies treating the articles with a continuous spray of water or other suitable liquid heated to the desired vulcanizing temp. Each of these pats. describes an app.

Rubber-like materials from oils and sulfur chloride. V. VILLA. Brit. 273,029, April 1, 1926. Reaction of S chloride on vegetable or animal oils is effected in the presence of a catalyst consisting of depolymerized Cl-free "artificial rubber," in a closed vessel and preferably at temps. of 0°–15°. The reaction may be allowed to take place in molds for producing tennis balls, cores for vehicle tires, shock absorbers or other articles.

Rubber composition. H. P. BUTLER. Can. 276,353, Dec. 20, 1927. A surfacing compn. is made by dissolving 3–5 oz. crude rubber in 2 pints C_6H_6, adding 4–5 pints CCl_4 and cooking the mixt. for 2–3 hrs., after which pyroxalin is added.

Rubber articles from latex. RUBBER LATEX RESEARCH CORPORATION. Brit. 273,991, Feb. 14, 1927. A jet of latex is coagulated in contact with acid, *e. g.*, 20–30% HOAc, the superficially coated material is allowed to stand until the coagulation proceeds throughout, and the product is pressed, washed and dried. An app. is described.

Apparatus for mixing, masticating, working or kneading rubber, etc. R. C. LEWIS and FARREL FOUNDRY & MACHINE CO. Brit. 273,455, June 2, 1926.

Electrodeposition of rubber. P. SCHIDROWITZ. Brit. 273,662, July 5, 1926. Articles are produced and fabrics are impregnated by electrodeposition of vulcanized rubber by methods as described in Brit. 193,451 (*C. A.* **17,** 3430) and Brit. 208,235 (*C. A.* **18,** 1589). A mold may be connected as anode in a 30% vulcanized latex and a current d. of 0.8–1.0 amp. per sq. dcm. maintained. A porous layer may be placed before the anode and fillers and dyes may be added to the latex.

Vulcanizing rubber footwear. L. CANDEE & CO. Brit. 274,357, Jan. 15, 1927. Articles such as footwear covered with a soft tacky vulcanizable varnish are given a hard finish by treatment with a halogen or a halogen S compd. such as Cl, Br, S chlorides, sulfuryl chloride, thionyl chloride or Se oxychloride. The varnish used preferably contains an oxidizable or drying oil. An app. is described.

Regenerating vulcanized rubber. C. O. CARLSSON. Brit. 274,387, March 15, 1927. Vulcanized rubber is dissolved in tar oil, impurities are removed by centrifuging or otherwise and the rubber is pptd. from the soln. by adding alc. or other suitable reagent.

Sheet material containing rubber. E. C. VILLIERS. Brit. 273,961, Dec. 8, 1926. A filler such as powd. asbestos, bitumen, C black, chalk, kieselguhr, lime, portland cement, "sulfur talc," dried or baked clay or sand, is mixed with coal-tar naphtha or other rubber solvent to form a pasty mixt. and there is added to this rubber latex or a similar latex. The order of mixing also may be reversed. After preliminary stirring and coagulation, the material is rolled into sheets, which may be reinforced with fabric or wire netting, and if S is present vulcanization by heating may be effected.

Molding ebonite. A. FRASER and R. and F. RISSIK, FRASER & CO., LTD. Brit. 273,355, Feb. 2, 1926. Undercured ebonite dust is placed in molds and subjected to a pressure exceeding 500 lbs. per sq. in. and heated to 220–250° for a short time, and allowed to cool before removing from the mold. Ni or other metals may be embedded in the material.

"Catgut substitutes." DUNLOP RUBBER CO., LTD., R. TRUESDALE, R. C. SMITH and E. SIMPSON. Brit. 273,896, July 7, 1926. Threads of silk, ramie, cotton or wool are impregnated with solns. such as those of cellulose, rubber, gutta percha or balata and twisted. An app. is described. Cf. *C. A.* **22,** 165.

Liquid rubber composition. H. P. BUTLER. Brit. 274,742, Feb. 2, 1927. A strongly adhesive compn. suitable for coating fabrics is formed by dissolving crude rubber in a solvent such as C_6H_6, with or without CCl_4, and heating to about 100° for 2–3 hrs. Gums such as damar, copal or kauri gum, drying oils and nitrocellulose may also be added, as may also various thinners and driers. Cf. *C. A.* **21,** 3489; **22,** 2081.

Rubber composition. HARRY L. FISHER. U. S. 1,668,235, May 1. Raw rubber is treated with *p*-toluenesulfonic acid (suitably at a temp. of about 110° or higher) to produce a reaction product which may be used for making molded articles. U. S. 1,668,236 specifies treating rubber 100 (in the absence of a solvent) with H_2SO_4 of 1.94 sp. gr. 2–25 parts to form a thermoplastic product.

Rubber composition. H. L. FISHER. U. S. 1,668,237, May 1. Rubber is heated with a mixt. of H_2SO_4 and *p*-toluenesulfonic acid in the relative proportions of 100: 8:2 and suitably at a temp. of about 88–130° to form a thermoplastic product suitable for making phonograph records, etc.

Rubber dispersion. H. L. TRUMBULL and J. B. DICKSON. U. S. 1,668,879, May 8. A viscous paste is formed from glue, casein or gluten, this is masticated and rubber is added, while the mastication is continued, in such large quantities as to produce a dispersion of the paste in the rubber, and the phase of the dispersion is then inverted to bring the paste into the continuous phase. The product thus obtained is similar to latex.

Reclaiming rubber. L. T. SMITH. Brit. 274,797, July 20, 1926. The material is treated with a solvent b. 160–200° such as a fraction of pine wood ext. consisting mainly of dipentene and contg. also pinene, terpinene, terpinolene and other terpenes.

Printing on rubber with colored rubber solutions. S. SAUL. Brit. 275,298, Jan. 6, 1927.

Paper for backing sheet rubber. G. E. GRIMM. U. S. 1,667,853, May 1. A backing for sheet rubber such as that used for patching rubber tires comprises paper carrying a smooth even coating of shellac or other hard resin mixed with a soft resin such as colophony and with castor oil or other suitable vegetable oil. Alc., turpentine and CH_2O also may be added. U. S. 1,667,854 specifies coating paper with waterglass, dextrin and glycerol, and then with rubber.

Articles of hard rubber. W. B. WESCOTT. U. S. 1,668,475, May 1. In forming abrasive wheels or other articles, a mixt. is made from comminuted old rubber, abrasive materials in granular form, S, and latex soln.; this mixt. is dried, molded and vulcanized.

Compositions containing rubber and cellulose derivatives. P. ALLMAN, H. N. MORRIS AND L. H. MARLOR. Brit. 274,968, April 30, 1926. Rubber is dissolved in one or more of the volatile hydrogenated products of aromatic hydrocarbons or their hydroxy compds. or ketones or isomers or esters of such compds., *e. g.*, cyclohexanone, and mixed with a soln. of cellulose derivs. such as cellulose nitrate or acetate. Nonvolatile hydrogenated aromatic hydrocarbons such as *ar*-tetrahydrohydronaphthol may be used as softening agents.

Vulcanizing rubber to leather. L. B. CONANT. Brit. 275,194, July 29, 1926. The leather is preheated to about the temp. of vulcanizing and the rubber is attached by heat and pressure.

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Effect of Heat on Raw Rubber[1]

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A study has been made of the effect of heat upon crude rubber. Heating in steam for 24 hours at 158° C. plastifies the rubber to about the same extent as about five passes through a tight mill. The chemical characteristics are changed in such a way as to indicate that a portion of the protein materials and fatty acid esters has been hydrolyzed. The rate of cure is increased in the case of most crudes for mercaptobenzothiazole and pure-gum mixes, but is less affected in the case of hexamethylenetetramine, diphenylguanidine, and ethylidene aniline. The stress-strain curve is affected by the heating in such a way as to make it more convex toward the strain axis.

A study has been made of the chemical constituents of the heated rubber which have been responsible for changes in curing characteristics. It is believed that the amines, nitrogen bases, and alkaloids are the principal active material responsible for the peculiarities of heated rubber.

Effect on Plasticity

IN THE report of the Physical Testing Committee[2] and in a communication by one of the writers,[3] it is pointed out that when rubber is milled upon rolls of relatively

[1] Presented before the Division of Rubber Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] IND. ENG. CHEM., **17**, 535 (1925).

[3] Park, *Rubber Age (London)*, **5**, 630 (1925).

high temperature a less plastic milled product is obtained than when the rolls are cold. The high temperature of the mill results in a temporary softening, which makes the rubber less susceptible to the mechanical action of the rolls. The result of this behavior is that any permanent effect of heat per se during milling on hot rolls is completely masked by the enormously greater effect of the mechanical action.

It has been stated by Worthington and Hyde[4] that when raw rubber is heated in steam at 10 to 60 pounds pressure for 7 hours the plasticity is increased. It is of interest to know whether the plasticizing effect so obtained is of the order of magnitude of that obtained by milling and whether the heating during milling is a small contributing factor to the permanent plasticity.

Several samples of rubber were heated in a small autoclave with water, care being taken to sweep out the air with steam. The heating was continued for periods of one day and the samples were then air-dried to transparency. In each case an increase in plasticity was obtained over the original sample.

Table I gives comparisons of the behavior of the rubber with various heat treatments and milling. A uniform sample of smoked sheet which had been blended in a large batch on an 80-inch (203-cm.) mill was used.

Table I—Effect of Various Heat Treatments and Milling on Plasticity

Method of Heat Treatment[a]	Passes through Cool Mill at 1 mm. Gage	Plasticity	Recovery
		Min.	*Min.*
Control		4.75	0.63
No treatment			
Steam		3.69	0.26
Dry (in press)	0	3.81	0.19
	1	4.38	0.42
	2	4.27	0.33
	3	4.15	0.25
	4	3.96	0.19
	5	3.69	0.16
	6	3.64	0.11

[a] At 158° C. and 5 kg. per sq. cm. (70 lbs.) pressure for 24 hours.

Plasticity is the thickness in millimeters of a 2-cc. pellet after 3 minutes at 70° C. under a 5-kg. load in the Williams plastometer. Recovery is the increase in thickness when measured immediately after removal from the press.

It may be seen that the increase in plasticity occurs whether or not the heating is done in the presence of steam and that the breakdown corresponds roughly to about four or five passes through a fairly tight mill.

Effect on Chemical Characteristics

At this point in the investigation it was discovered that a pronounced increase in rate of cure of the rubber was brought about by the heating. This effect was noted in two mixes; in one the time of cure was reduced from 3 hours at 141° C. to less than 2½ hours at 141° C., and in the other, from 45 minutes at 125° C. to less than 30 minutes at 125° C. The heated rubber was always foul in odor and when fresh from the

[4] U. S. Patent 1,360,486 (1920).

autoclave sometimes smelled decidedly of amines and ammonia. It was thought that protein hydrolysis was responsible for the odor and the increased rate of cure, and so a more comprehensive series of experiments was carried out to get a more accurate idea of the changes taking place in the rubber and the effect of these changes upon cure with various accelerators.

The apparatus consisted of a steel autoclave 13 inches (33 cm.) deep by 8 inches (20 cm.) in diameter capable of holding 8 to 10 kg. of crude rubber. It was provided with a bolted-on lid, lead gasket, and blow-off valve. About 1 liter of water was added. The autoclave was placed in a horizontal pot heater and heated for 10 minutes at 158° C. in steam. The heater was then opened and the blow-off valve of the autoclave opened for 5 minutes to allow steam to drive out the air present when the autoclave was charged. The blow-off valve was then shut, the heater closed, and the rubber heated for 24 hours at 158° C.

In Table II is presented the effect of this heat and steam treatment on several different types of rubber. The first effect of heating noted is the increase in the acetone extract, which may be due to partial depolymerization of the rubber itself, thus rendering it acetone-soluble. Another source of increased acetone extract may be the protein hydrolysis products. The second effect is the increase in acid number, as determined on the acetone extract by the method of Whitby and Winn.[5] This is probably caused by the effect of heat, pressure, and steam in hydrolyzing the fatty acid esters (glycerol salts of the fatty acids[6]), and also by the hydrolysis of the rubber protein and formation of free amino acids. The third effect is the increase in the acetone-soluble nitrogen at the expense of the acetone-insoluble, and may be caused, as previously stated, by an increased solubility in acetone of the protein hydrolysis products over the original rubber proteins. It should also be noted that the total nitrogen after heating is in all cases less than before heating, showing that the ammoniacal odor on opening the autoclave was really due to volatile nitrogenous substances.

Effect upon Cure

A more thorough investigation of the effect of heating rubber was next undertaken. Several different types of rubber in five different mixes were cured and complete physical data were obtained. These data are so voluminous that only a brief summary can be given. (Tables III and IV)

PURE-GUM MIX, NO ACCELERATOR—Table III presents the summarized data obtained in a pure-gum mix. All the different types of rubber are shown to increase in rate of sulfur combination

[5] *J. Soc. Chem. Ind.*, **42**, 336T (1923).

[6] Lewkowitz, "Chemical Examination of Oils, Fats, and Waxes," 5th ed., Vol. I, p. 77.

Table II—Effect of Heat on Various Types of Rubber

Rubber	Acetone Extract		Acid Number		N_2 in Extract		N_2 in Residue		Plasticity	
	Before	After	Before	After	Before	After	Before	After	Before	After
					%	%	%	%	*Mm.*	*Mm.*
Pale crepe T	3.09	3.86	231	300	0.05	0.16	0.41	0.34	466	331
Roll brown S A	1.60	2.72	109	163	0.08	0.15	0.47	0.31	367	253
Smoked sheet V V	1.60	1.96	236	311	0.168	0.292	0.47	0.29	...	...
Acetone-extracted smoked sheet V V	0.71	1.88	...	...	...	0.13	...	0.23	353	285
Smoked sheet S S	3.13	4.28	253	305	0.24	0.38	0.58	0.40	565	345
Sprayed latex C	3.46	5.82	381	411	0.13	0.20	0.56	0.38	502	282
Sprayed latex C, H_2O extracted	2.37	4.29	265	333	0.19	0.39	0.75	0.50	...	...
Evaporated latex	3.56	7.65	...	...	0.12	0.33	0.56	0.26	399	266

Table III—Effect of Heat on Cure of Pure-Gum Stock (100 Rubber, 10 Sulfur)

Rubber Sample	Time of Cure		Vulcanization Coefficient				Modulus at 800%			
			1:30 at 141° C.		2:00 at 141° C.		Best Cure		2:15 at 141° C.	
	Before	After	Before	After	Before	After	Before	After	Before	After
Pale crepe T	2:15	2:00−	1.42	1.96	1.90	2.49	39	28	39	34
Pale crepe S A	2:15+	2:15−					49	36	49	36
Roll brown Q	1:45+	1:30−[a]					80	97	146	190
Roll brown D D	2:00−	1:30−	2.52	3.96			74	98	124	142
Roll brown S A	2:00	1:45+					84	76	102	110
Smoked sheet V V	2:15	2:00					53	38	53	42
Smoked sheet S S	2:00	1:45	2.29	2.49			75	48	96	68
Water-extracted sprayed latex C	1:45[b]	1:45[b]			5.95[c]	6.10[c]			(1:45 cure) 134	88
Sprayed latex C	1:45[b]	1:45[b]	...	...	6.10[c]	7.20[c]			151	188

Stiffness Index				Tensile (kg. per sq. cm.)				Elongation (per cent)			
Best Cure		2:15 at 141° C.		Best Cure		2:15 at 141° C.		Best Cure		2:15 at 141° C.	
Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
23	13	23	17	117	122	117	135	1000	1030	1000	1010
29	19	29	19	124	125	124	125	960	985	960	985
53	67	101	146	155	154	190	210	920	870	850	810
48	68	76	100	120	140	154	149	880	860	840	805
55	50	70	76	152	160	164	174	900	910	880	875
33	21	33	22	117	125	117	138	935	995	935	980
48	20	64	34	139	141	158	178	905	970	885	940
		(1:45 cure)				(1:45 cure)					
		94	57			162	190			935	915
		113	142			200	194			845	810

[a] Lowest cure obtained; best cure is probably definitely lower. [b] All overcured; 1:45 was shortest cure obtained.
[c] 2:15 cure at 141° C.

after heating. This checks the hand observation of time of cure based largely on tear, which is given in columns 2 and 3. In spite of this fact the modulus at 800 per cent and the stiffness index have decreased except in the case of roll brown crepe, even at the same time of cure. Examination of the tensile and elongation figures shows that the last part of the stress-strain curve is as high for the heated sample as for the original. This change in the form of the stress-strain curve is discussed later. It should be noted in this table, as well as in most of those following, that roll brown crepes show different physical properties than the other types of rubber investigated. If the stress-strain curve is plotted, that of roll brown crepe will be found to be much steeper than any of the others. Thus the stiffness index (difference between modulus at 600 and 800 per cent elongation) of roll brown is usually increased considerably by the heat treatment. Other rubbers may not show this increase in stiffness index, because the curve is flatter at the 600 to 800 per cent elongation, but may have tensiles at break equal or superior to those of roll brown crepe.

The best cures for sprayed latex were not obtained, the 1 hour and 30 minute cure being overvulcanized. In the case of the water-extracted sample both the stiffness index and modulus are lowered by heating, while in the unextracted sample they are increased. This may be due to the fact that the rate of cure was but little increased in the extracted sample and enormously increased in the unextracted. The combined-sulfur figures are evidence of the truth of this statement. It is, of course, obvious that a water-soluble material has been removed, which on hydrolysis is a strong accelerator of vulcanization.

MERCAPTOBENZOTHIAZOLE ADDED AS ACCELERATOR (Table IV)—*Formula 1.* This formula is the one used by Dinsmore and Zimmerman,[7] which cures an average crepe or sheet rubber in 1 hour at 125° C. (20 pounds or 1.4 kg. per sq. cm. steam).

Formula 2. At this time and with this accelerator it occurred to the writers to study the effect of time of heating and the effect of dry heat as compared with moist heat. Using Formula 2, three samples of smoked sheets, all taken from the same piece of rubber, were heated as stated. It is evident that the cure effect increases with time of heating. In the case of the sample heated dry in a mold, the cure effect is present although weak. In this sample, as in those heated wet, the effect of heat shows up in the plasticity figures and in the form of the stress-strain curve.

In this case also, the rate of cure and sulfur combination is increased; the rate of physical cure is also increased as judged by hand tests with emphasis on tear. The general position of the stress-strain curves is changed toward the load axis by heating, except in the case of sprayed latex. The combined-sulfur figures show that heating has little, if any, effect upon the rate of cure of sprayed latex, while the lowering of the modulus and stiffness index is peculiar to this type of rubber. It seems probable that the high stiffness index of the roll brown rubbers as well as the sprayed latex may be explained as in the discussion of Table III and in a later section of this paper. The low stiffness index of pale crepe T might be open to question but for the fact that the time-stiffness curve at 700 per cent is almost flat at this point, increasing only 4 in 30 minutes additional cure.

HEXAMETHYLENETETRAMINE ADDED AS ACCELERATOR—The most noticeable feature of these data is the definite lowering of physical properties in smoked sheets after heating and the accompanying movement of the stress-strain curves toward the axis of elongation. The same effect is true in a lesser extent of roll brown crepe, but barely noticeable in pale crepe.

DIPHENYLGUANIDINE ADDED AS ACCELERATOR—The effect

[7] IND. ENG. CHEM., 17, 144 (1926).

Table IV—Effect of Heat on Cure of Stock Containing Accelerators

Rubber Sample	Time of Cure		Coefficient of Vulcanization				Modulus at 700%				Stiffness Index[g]				Tensile (kg. per sq. cm.)				Elongatio	
			30-min. cure		1-hour cure		best cure		1-hour cure		best cure		1-hour cure		best cure		1-hour cure		best cure	
	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
MERCAPTOBENZOTHIAZOLE (FORMULA 1—100 RUBBER, 6 ZNO, 3.2 SULFUR, 0.35 MERCAPTOBENZOTHIAZOLE)																				
			(Cure at 125° C.)				(Cure at 125° C.)				(Cure at 125° C.)				(Cure at 125° C.)				(Cure at	
Pale crepe T	1:00	:30[a]	0.82	1.52	1.22	2.19	60	90	60	104	41	68[a]	41	77	169	206	169	220	890	840
Pale crepe S A	1:00	:30−[a]					76	96	76	116	53	72[a]	53	86	167	194	167	208	845	830
Roll brown Q	1:00	:30−[a]					106	218	106	224	74	161[a]	74	...	167	246[a]	167	250	780	725
Roll brown D D	1:30[b]	:30−[a]	1.20	2.33			54[b]	180[a]	47	212	35[b]	132[a]	29	...	112[b]	219[a]	95	220	840[b]	740[a]
Roll brown S A	1:00	:30−[a]					94	152[a]	94	210	66	114[a]	66	155	162	204[a]	162	216	800	760
Smoked sheet V V	1:00−	:30+					91	94	91	116	68	70	68	86	178	200	178	208	820	825
Smoked sheet S S	:45	:30[a]		1.58			105	108	112	129	75	81[a]	79	95	180	208	187	198	800	810
Water-extracted sprayed L C	:30	:30−					(30 at 20)		(30 at 20)											
	Overcured		1.61	1.73	2.20	2.23	169	132	190	142	119	96	130	100	200	210	230	200	740	790
Sprayed L C	:30	:45	1.45	1.63	2.03	2.26	171	146	192	146	119	109	133	109	204	224	238	206	740	785
MERCAPTOBENZOTHIAZOLE (FORMULA 2—100 RUBBER, 2.75 SULFUR, 3.0 ZNO, 0.5 MERCAPTOBENZOTHIAZOLE)																				
Smoked sheet spl.	:30	:30−[a]					76	115[a]	100	147	54	89[a]	73	112	176	210[a]	176	230	860	800[a]
Smoked sheet[e]	:30	:30−[a]					76	145[a]	100	194	54	115[a]	73	154	176	230	176	240	860	775
Smoked sheet[d]	:30	:30[a]					76	80	100	96	54	60	73	71	176	190	176	192	860	840
Acetone-extracted smoked sheet VV[f]	....	....							80	170			56	120			150	212		
Acetone-extracted pale crepe P[e,b]	:45	:20−[a]					60	81	72	133	41	62[a]	50	103	140	180	140	195	810	825
HEXAMETHYLENETETRAMINE (100 RUBBER, 6 ZNO, 3 SULFUR, 0.9 HEXA)																				
			(Cure at 141° C.)				(Cure at 141° C.)				(Cure at 141° C.)				(Cure at 141° C.)				(Cure a	
Pale crepe T	1:00	1:00+	0.53	0.63	0.98	1.19	66	54	66	54	46	37	46	37	178	177	178	177	880	900
Pale crepe S A	1:00	1:00−					74	66	74	66	52	46	52	46	166	181	166	181	855	870
Roll brown Q	1:00−	1:00					158	118	158	118	113	85	113	85	205	197	205	197	759	795
Roll brown D D	:45+	:45+	0.99	1.23			111	88	140	140	77	62	98	100	162	164	176	194	770	815
Roll brown S A	1:00	:45+					74	51	74	78	51	34	51	54	142	130	142	172	835	870
Smoked sheet V V	1:00	1:00−					83	67	83	67	59	46	59	46	174	161	174	161	835	850
Smoked sheet S S	:45+	:45+	0.83				79	60	111	75	55	41	79	51	158	146	182	156	830	865
Water-extracted sprayed latex C	:45	:30+	1.11	1.38	2.21	2.23	144	66	156	181	100	44	108	82	188	134	195	173	755	835
Sprayed latex C	:45	:30+	1.11	1.21	2.28	2.42	143	71	175	120	98	51	120	89	202	150	222	204	775	845
DIPHENYLGUANIDINE (100 RUBBER, 6 ZNO, 2.75 SULFUR, 0.4 D.P.G.)																				
Pale crepe T	1:00−	1:00	0.68	0.87	1.18	1.50	75	46	75	46	54	30	54	30	168	144	168	144	840	880
Pale crepe S A	1:00−	1:00					78	58	78	58	56	40	56	40	178	136	178	136	845	870
Roll brown Q	1:00	1:00					106	74	106	74	75	52	75	52	166	132	166	132	785	800
Roll brown D D	1:00+	1:00+	0.98	1.18			81	64	81	64	56	43	56	43	134	120	134	120	790	825
Roll brown S A	:45	1:00+					82	75	104	75	57	52	74	52	164	144	179	144	830	820
Smoked sheet V V	1:00−	1:00−					102	78	102	78	73	54	73	54	168	159	168	159	790	830
Smoked sheet S S	:45+	:45+	0.95	0.88			104	50	118	60	73	33	84	40	173	124	189	129	800	855
Water-extracted sprayed latex C	:45	:45	1.34	1.35	2.26	2.22	146	95	168	116	102	65	119	80	194	150	200	160	760	785
Sprayed latex C	:30+	:30	1.23	1.46	2.10	2.20	110	85	173	105	79	62	124	77	175	157	220	190	790	810
ETHYLIDINE ANILINE (100 RUBBER, 6 ZNO, 3 SULFUR, 0.35 ETHYLIDINE ANILINE)																				
Pale crepe T	1:00	1:00	0.85	1.27	0.78	1.31	64	35	64	35	44	22	44	22	158	132	158	132	870	930
Pale crepe S A	1:00	1:00					80	37	80	37	57	24	57	24	176	133	176	133	845	915
Roll brown Q	1:30+[b]	1:30+[b]					54	36	43	24	35	22	28	13	102	108	103	80	830	905
Roll brown D D	:45	1:00	1.20				36	77	36	77	21	55	21	55	80	140	67	140	855	805
Roll brown S A	1:00	1:00					82	73	82	73	56	50	56	50	165	148	165	148	825	830
Smoked sheet V V	1:00	1:00					80	49	80	49	57	33	57	33	150	130	150	130	920	870
Smoked sheet S S	:45	:45					83	39	83	46	59	25	59	30	158	112	158	126	825	880
Water-extracted sprayed latex C	:45−	:45−	1.30	1.50	2.35	2.32	135	82	148	90	94	56	101	61	190	152	186	155	765	815
Sprayed latex C	:30	:30	1.37	..	2.14	2.27	110	92	152	109	80	67	106	80	171	173	193	188	790	820

[a] Lowest cure obtained.
[b] Highest cure obtained.
[e] Heated in autoclave 5 days.
[d] Heated in mold in press 1 day at 158° C.
[e] Heated 39 hours at 158° C.
[f] 1 part stearic acid added.
[g] Stiffness index for these stocks is th
modulus between 700 and 500 per cent elo

Heat on Cure of Stock Containing Accelerators

Modulus at 700%			Stiffness Index[g]				Tensile (kg. per sq. cm.)				Elongation (per		
T CURE	1-HOUR CURE		BEST CURE		1-HOUR CURE		BEST CURE		1-HOUR CURE		BEST CURE		1-HOU
re After	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After	Before
MULA 1—100 RUBBER, 6 ZNO, 3.2 SULFUR, 0.35 MERCAPTOBENZOTHIAZOLE)													
(Cure at 125° C.)			(Cure at 125° C.)				(Cure at 125° C.)				(Cure at 125° C		
90	60	104	41	68[a]	41	77	169	206	169	220	890	840	890
96	76	116	53	72[a]	53	86	167	194	167	208	845	830	845
218	106	224	74	161[a]	74	...	167	246[a]	167	250	780	725	780
180[a]	47	212	35[b]	132[a]	29	...	112[b]	219[a]	95	220	840[b]	740[a]	835
152[a]	94	210	66	114[a]	66	155	162	204[a]	162	216	800	760	800
94	91	116	68	70	68	86	178	200	178	208	820	825	820
108	112	129	75	81[a]	79	95	180	208	187	198	800	810	795
at 20)	(30 at 20)												
132	190	142	119	96	130	100	200	210	230	200	740	790	745
146	192	146	119	109	133	109	204	224	238	206	740	785	750
MULA 2—100 RUBBER, 2.75 SULFUR, 3.0 ZNO, 0.5 MERCAPTOBENZOTHIAZOLE)													
115[a]	100	147	54	89[a]	73	112	176	210[a]	176	230	860	800[a]	800
145[a]	100	194	54	115[a]	73	154	176	230	176	240	860	775	800
80	100	96	54	60	73	71	176	190	176	192	860	840	800
	80	170			56	120			150	212			805
81	72	133	41	62[a]	50	103	140	180	140	195	810	825	810
ETETRAMINE (100 RUBBER, 6 ZNO, 3 SULFUR, 0.9 HEXA)													
(Cure at 141° C.)			(Cure at 141° C.)				(Cure at 141° C.)				(Cure at 141° C		
54	66	54	46	37	46	37	178	177	178	177	880	900	880
66	74	66	52	46	52	46	166	181	166	181	855	870	855
118	158	118	113	85	113	85	205	197	205	197	759	795	750
88	140	140	77	62	98	100	162	164	176	194	770	815	745
51	74	78	51	34	51	54	142	130	142	172	835	870	835
67	83	67	59	46	59	46	174	161	174	161	835	850	835
60	111	75	55	41	79	51	158	146	182	156	830	865	795
66	156	181	100	44	108	82	188	134	195	173	755	835	745
71	175	120	98	51	120	89	202	150	222	204	775	845	750
ANIDINE (100 RUBBER, 6 ZNO, 2.75 SULFUR, 0.4 D.P.G.)													
46	75	46	54	30	54	30	168	144	168	144	840	880	840
58	78	58	56	40	56	40	178	136	178	136	845	870	845
74	106	74	75	52	75	52	166	132	166	132	785	800	785
64	81	64	56	43	56	43	134	120	134	120	790	825	790
75	104	75	57	52	74	52	164	144	179	144	830	820	795
78	102	78	73	54	73	54	168	159	168	159	790	830	790
50	118	60	73	33	84	40	173	124	189	129	800	855	785
95	168	116	102	65	119	80	194	150	200	160	760	785	735
85	173	105	79	62	124	77	175	157	220	190	790	810	760
E (100 RUBBER, 6 ZNO, 3 SULFUR, 0.35 ETHYLIDINE ANILINE)													
35	64	35	44	22	44	22	158	132	158	132	870	930	870
37	80	37	57	24	57	24	176	133	176	133	845	915	845
36	43	24	35	22	28	13	102	108	103	80	830	905	880
77	36	77	21	55	21	55	80	140	67	140	855	805	820
73	82	73	56	50	56	50	165	148	165	148	825	830	825
49	80	49	57	33	57	33	150	130	150	130	820	870	820
39	83	46	59	25	59	30	158	112	158	126	825	880	825
82	148	90	94	56	101	61	190	152	186	155	765	815	745
92	152	109	80	67	106	80	171	173	193	188	790	820	750

C.

[a] Heated 39 hours at 158° C.
[b] 1 part stearic acid added.

[g] Stiffness index for these stocks is the differen modulus between 700 and 500 per cent elongation.

GATION (per cent)		
RE	1-HOUR CURE	
After	Before	After
ure at 125° C.)		
840	890	825
830	845	795
725	780	690
740[a]	835	700
760	800	710
825	820	785
810	795	775
790	745	755
785	750	785
800[a]	800	775
775	800	775
840	800	810
	805	840
825	810	755
ure at 141° C.)		
900	880	900
870	855	870
795	750	795
815	745	760
870	835	850
850	835	840
865	795	850
835	745	770
845	750	790
880	840	880
870	845	870
800	785	800
825	790	825
820	795	820
830	790	830
855	785	825
785	735	765
810	760	800
930	870	930
915	845	915
905	880	905
805	820	805
830	825	830
870	820	870
880	825	870
815	745	800
820	750	790

the difference in elongation.

of heating was definitely to lower the quality of the diphenylguanidine stocks in every case. The samples also had a decidedly poorer tear than the originals, as well as lower tensile and modulus. The rate of cure, judged by hand tests and combined sulfur, was unaffected.

ETHYLIDINE ADDED AS ACCELERATOR—The effect on these stocks is similar to the effect on diphenylguanidine stocks. The rate of cure as judged by hand tests and combined sulfur was not increased. The stress-strain curves approach the strain axis and the physical properties are lower in all cases except that of roll brown crepe D D, which could not be repeated owing to loss of the sample.

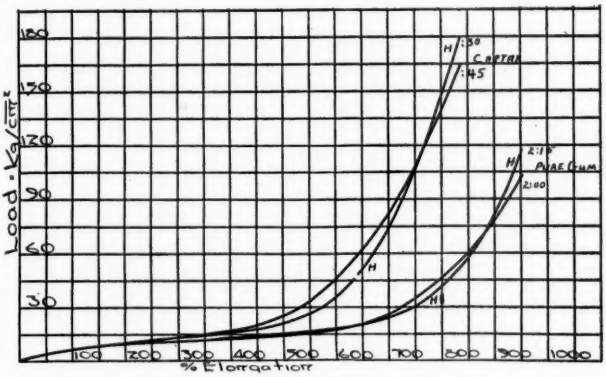


Figure 1

On summing up the effect of heating upon the cure with various accelerators, there appear to be two separate and entirely independent influences at work. The first of these factors seems to be strictly chemical in its nature and its effect is noted by: (1) increase in acetone extract and change in nitrogen distribution, as shown in Table II; (2) acceleration of cure, especially in the case of mercaptobenzothiazole; (3) failure of acetone to remove the body which undergoes change on treating; and (4) removal by water of a portion of the material which undergoes change. The second factor seems to be physical and is possibly due to an altered structural condition. It is perhaps closely connected with the greater plasticity of the uncured rubber.

The effect on the cured rubber may be summed up as follows:

(1) There is a tendency to produce a softer stock with a somewhat different form of stress-strain curve.

(2) The explanation of the low results with diphenylguanidine and ethylidene aniline is not to be found in the poorer innate qualities of the rubber, for the same heated samples produced satisfactory results in other mixes. The phenomenon may be due to the specific action of certain substances. Extra amounts of stearic acid in the presence of ZnO do not increase the rate of sulfur combination, but do greatly improve certain physical properties. Additional free fatty acids are probably formed by heating, as noted in Table II.

(3) The cure effect is present to a greater extent in the presence of an excess of moisture over that found in the rubber, pointing to hydrolytic action.

Effect of Heating upon the Stress-Strain Curve

As was stated in the discussion of Table III, a difference in the form of the stress-strain curve was noted on all heated rubbers. Regardless of whether the general change in position of the curves has been toward or away from the strain axis (whether the modulus and tensile have been lowered or raised by heating), if a single curve of each stock can be found in the same general position on a stress-strain chart, the one made from the heated rubber will have a greater convexity toward the strain axis. In other words, that portion of the curve below 800 per cent elongation in pure gum and below 600 per cent in accelerated stocks is flatter after heating than in unheated rubber. At lower elongation or just before break the heated rubber may have a slightly higher modulus than the unheated; but during the middle part the arc of the curve swings farther to the right. This is noticeable in nearly all the curves, and is shown in Figure 1.

Sometimes the difference is striking. In other cases it would not be noticed upon casual inspection, but in 90 per cent of a very large number of comparisons it was possible to pick the heated rubber from the shape of the stress-strain curve. It is interesting to note that the difference in shape persists after 9 days' aging in the Geer oven, 16 hours in the Bierer-Davis oxygen bomb, and 1 year natural aging.

Note—As was stated in the discussion of Table III, a difference in the form of the stress-strain curve was noted between roll brown crepe and the other types of rubber investigated. A typical cure for brown crepe seems to be a shorter stress-strain curve giving a much steeper slope at the proper tensile. If brown crepe is cured to give the same slope as pale crepe or smoked sheet rubber it is undercured and flabby.

A sample of smoked sheet heated dry showed the same type of curve. Whether this type of curve is more or less desirable than the type which more nearly approaches Hooke's law is an open question. A rubber of this type deforms easily up to a certain point and suddenly becomes exceedingly stiff and very difficult to break.

Whatever other changes may have taken place upon heating, it is obvious that the proteins were profoundly affected. Undoubtedly, hydration and hydrolysis took place to a large extent. It is fairly well known that rubbers having widely different degrees of protein hydration may be prepared from the same latex. Those containing highly hydrated protein are softer in texture than those of low hydration. This fact probably explains the greater plasticity of the rubber before milling and curing. It is possible that the hydrated rubber is less severely broken down during milling owing to the allowance by the protein of greater slippage between the structural units. In this case the structure of the finished cured sheets of heated rubber would be more like the original structure than the unheated ones. It must be admitted that the suggested explanation is given upon a basis of very

Table V—Action of Protein Products on Rate of Cure

Class	Material	Pure Gum	Mercapto	Other Accelerators
Amino acids:				
Monoaminomonocarboxylic	Alanine, glycine	No action	Marked stiffening action	
Monoaminodicarboxylic acid	Aspartic acid	No action	No action	
Amino acid containing phenyl group	Tyrosine	No action	No action	
Sulfur containing amino acid	Cystine	No action	No action	
Nitrogeneous bases:				
Heterocyclic	Quinoline	No action	Stiffens but does not accelerate	Vulcone, same as mercapto
	Creatine	No action	Stiffens but does not accelerate	Vulcone, same as mercapto
Aliphatic	Tri-*n*-propylamine	No action	Slight activation	
Putrefactive bases: tetramethylenediamine[a] (putrescine)		Accelerates and stiffens	Activates and stiffens	
Proteins: hydrolysis products	Hydrolyzed glue	Accelerates and stiffens	Activates and stiffens	Activates and stiffens all accelerated stocks tried
	Peptone	Accelerates and stiffens	No action	Activates and stiffens hexa, D. P. G., no action in Vulcone
Carbohydrates	Starch	No action		
	Sugar	Slight retarder		
Glucosides	Saponin	Retarder in all cases		
Tannin	Non-glucosidal tannin	No action	Activates	
Enzymes	Fleischman's yeast	No action	Activates	

[a] A stiffer stock is obtained in 5 minutes at 141° C. with 1 per cent of this material than is obtained in 150 minutes at 141° C. without it (unpublished report by W. W. Vogt).

incomplete facts, but it is believed to be warranted in view of the current interest in the spheroidal theory.

Differences of this kind in the type of the stress-strain curve are frequently met in the study of pigments. They have been noted by the authors in the case of both zinc oxides and carbon blacks.

Effect of Heating upon Aging

Although the aging studies were fairly comprehensive, no attempt has been made to arrive at more than qualitative conclusions. Three age tests were run on each stock: (1) 9 days in Geer oven at 70° C.; (2) 16 hours in Bierer-Davis oxygen bomb; (3) 1 year natural aging. In all cases heated rubbers were equal or superior to the unheated as judged by modulus, tensile, and elongation. A possible explanation of this is that heating causes the natural antioxidant to become more reactive, through some internal change in the rubber structure.

One rather remarkable feature of the diphenylguanidine stocks was that in several cases the year-old samples of heated rubber were equal to the unheated aged samples, although they were much inferior when fresh.

Cause of the Increase in Rate of Cure

A review of the literature shows that several investigators have noted changes in rate of cure due to various naturally occurring products. The data, while somewhat conflicting, are presented. Frank[8] claimed most amino acids to be without effect in rubber-sulfur mixes. Gorter[9] found that one amino acid, leucine, shortened the time of cure of a pure-gum mix from 115 minutes to 105 minutes. Eaton[10] investigated tyrosine, which proved to be without effect. Stevens[11] added peptone and casein to nearly nitrogen-free rubber and obtained almost as fast a cure as in the original rubber. Eaton[12] and also Eaton and Grantham[13] added peptone and casein to rubber-sulfur mixes without causing any acceleration. Recently Eaton and Bishop[14] found that, of several alkaloids tried, only one, emetine, had any marked accelerating value in a rubber-sulfur mix.

In the writers' study of the causes of increased rate of cure, they have attacked the problem from two standpoints: (1) the compounding of some of the known protein decomposition products and such other substances as were thought might be present in rubber; (2) a study of the water-extractable matter obtained after heating. The number of plant products which might be present in cured rubber is rather

[8] *Rubber Ind.*, **1914**, 144.
[9] *Arch. Rubbercultuur*, **1**, 377 (1917).
[10] *Malayan Agr. J.*, **6**, 319 (1918).
[11] *Kolloid-Z.*, **14**, 91 (1914).
[12] *Malayan Agr. J.*, **6**, 84 (1918).
[13] *J. Soc. Chem. Ind.*, **35**, 722 (1916).
[14] *Malayan Agr. J.*, **14**, 8 (1926).

appalling and includes alkaloids, amino acids, enzymitic products, carbohydrates such as sugar or starch, putrefaction bases, gums, waxes and resins, saponin, tannin, proteins with their intermediate and final decomposition products and other nitrogenous bases.

The writers were particularly interested in nitrogenous bodies, as the odor of the rubber on removal from the autoclave, as well as the nitrogen determinations as listed in Table II, indicated a profound change in the nature of the nitrogen-containing bodies.

ADDITION OF KNOWN PROTEIN DECOMPOSITION PRODUCTS—As a first step in determining what materials influenced the rate of cure or physical properties, several representative members of the different classes were compounded, cured, and tested. These materials were tested in a 100 rubber–10 sulfur mix using 0.5 to 1.0 per cent of substance being studied. Another series consisted of 100 rubber, 6 ZnO, 2.75 sulfur, 0.5 mercaptobenzothiazole, and 0.10 to 0.25 per cent of the natural product. The second formula was used because this accelerator is somewhat more sensitive to added materials than other commercial accelerators. Some of the materials were also tested in stocks containing other accelerators, such as Vulcone, diphenylguanidine, etc. The results of these tests are given in Table V.

The principal fact to be noted is that the best activators of accelerated stocks are the least complex molecules—e. g., glycine—while the best accelerators of the pure-gum mix are those in which there is a strong base, not impeded by an acid radical. (The hydrolyzed glue contained free amines.) The action of peptone is peculiar; it contained no free amines and simple amino acids, for it would then have activated the mercaptobenzothiazole cure, yet it apparently shares some property of hydrolyzed glue, to cause it to react in the same manner in a rubber-sulfur mix.

ISOLATION OF HYDROLYSIS PRODUCT OF NATURAL ACCELERATOR—Since such differences in rate of cure were noticed before and after heating rubber, it was believed that either the natural accelerator or a clue to its identity obtained by isolating its hydrolysis product might be isolated from a water or alcohol extract of the heated rubber. Acetone-extracted rubber was used since the action of the acetone-soluble constituents[15] was known and would therefore not hinder the study. The thinly milled smoked-sheet rubber, after acetone extraction, was heated in the autoclave with water as described under the section "Effect on Chemical Characteristics." The rubber was then sheeted out on a corrugated mill ("cracker") and the water extract thus obtained was united with the water taken from the autoclave. The sheeted-out rubber was rolled up in cloth which had been previously boiled out in water. The rubber was then soaked

[15] Whitby, *J. Chem. Soc.* (*London*), **1926**, 1448; also *Rubber Age* (*London*), **5**, 401 (1926).

in water at 80–90° C. until fresh water added daily did not become colored in 24 hours. Fifty pounds (23 kg.) of rubber were extracted in this way using about 50 liters of water, which was acidified to prevent loss of volatile bases and concentrated on the steam table to a volume of about 1.5 liters. To this were added the water taken from the autoclave and that removed from the hydrolyzed rubber while sheeting out.

On cooling this concentrated solution a brown, slimy precipitate settled out, which was not again soluble in water but was easily soluble in alcohol. This material resisted all attempts to purify it and remained a brown, molasses-like product, practically odorless.

The water solution was then further concentrated to a volume of about 500 cc. per 50 pounds (23 kg.) of rubber. No further crystallization took place on cooling, but by applying first a chloroform extraction and then the butyl alcohol extraction method of Dakin[16] the solution was divided into three parts: (1) chloroform-soluble, water-soluble; (2) butyl alcohol–soluble, chloroform-insoluble, water-soluble; (3) butyl alcohol- and chloroform-insoluble and water-soluble. A better understanding of this procedure may be obtained from Table VI. The apparatus used for the butyl alcohol extraction was of the Kutscher-Steudel[17] type and provides a method for the hot extraction of one liquid by another by constantly bringing fresh solvent into contact with the liquid being extracted. In these three solutions there may be present amino acids or other protein decomposition products, alkaloids, or other nitrogen bases; glucosides, carbohydrates, sugars, gums, and tannin. Water solutions of the above three fractions were prepared and tested by a large number of reagents for the above-mentioned substances. The following results were obtained:

1—No part of the hydrolysate contains any material that will reduce Fehling's solution, such as sugars, starch, and certain glucosides. Negative tests were obtained for tannin by several reagents, particularly those which would distinguish it from saponin. No free amines were found.

2—Positive tests were obtained for saponin, proteins, and other carbohydrates and their hydrolysis products with the Molisch test and others. Positive tests were also obtained for alkaloids and other nitrogen bases.

The resinous nature of the different fractions may be due to certain natural resins, waxes, and gums which are not soluble in acetone but are soaked out by water after hydrolysis. It now remained to separate and identify these products, if possible. No one fraction amounted to more than 0.1 per cent of the rubber, the greater part of the water extract being inactive, resinous material.

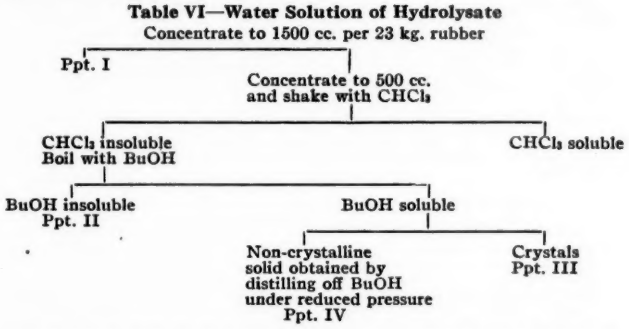
Alcohol as Extracting Medium. It was thought that the use of alcohol as an extracting medium might give separations

[16] *Biochem. J.*, **12**, 980 (1918).

[17] *J. Chem. Soc.* (*London*), **84**, 80A (1904).

which could be more easily purified than those from water. Therefore, a fresh lot of smoked sheets, about 25 pounds (11 kg.), was acetone-extracted, hydrolyzed, and then extracted with alcohol in a large metal extractor. On concentration the alcohol extract yielded a small quantity of flat, brownish crystals which could not be purified, as the water extract had yielded a similar, though slimy, precipitate. These crystals were numbered Ppt. I. The filtrate was next taken to dryness, no further crystallization having taken place, taken up in water in which the gummy residue was entirely soluble, and then extracted hot with butyl alcohol until fresh additions of the butyl alcohol were colorless. The chloroform extraction was omitted in this case and three products were obtained.

Table VI—Water Solution of Hydrolysate


Concentrate to 1500 cc. per 23 kg. rubber
Ppt. I
Concentrate to 500 cc. and shake with CHCl3
CHCl3 insoluble Boil with BuOH
CHCl3 soluble
BuOH insoluble Ppt. II
BuOH soluble
Non-crystalline solid obtained by distilling off BuOH under reduced pressure Ppt. IV
Crystals Ppt. III

Ppt. IV, butyl alcohol–soluble, non-crystalline material, which, according to the scheme of Dakin contains such amino acids as proline and other heterocyclic compounds. The writers have shown that quinoline, another heterocyclic compound, has a slight stiffening action on mercapto-accelerated stocks, much in the same order as this crude material. From this fraction Ppt. IV a white crystalline solid was obtained, which after repeated crystallizations from alcohol melted sharply at 205° C. The melting point of proline is 208° C. However, this substance analyzed to a C_4 compound, whereas proline is a C_5, and the writers were not able to identify it. The analysis was as follows: carbon, 44.72–45.30; hydrogen, 6.72–6.84; nitrogen, 12.03 per cent. Such a compound would have a formula of $C_4H_8O_2N$. There was not enough sample for a molecular weight determination.

Ppt. III, butyl alcohol–soluble, separates out as minute crystals on cooling. In the Dakin scheme these crystals are monoamino acids, and since they seemed very uniform under the microscope there were probably no other substances present. They melted at 164° C.

Ppt. II, butyl alcohol–insoluble, water-soluble, non-crystalline residue composed of diamino and dicarboxylic acids and a mixture of other plant substances.

When these materials were added to a mercapto stock in the proportion of 2 per cent on the rubber, the results shown in Table VII were obtained.

As will be noted, the addition of these substances activated mercapto and produced both a stiffer stock and a faster cure.

Fractions from Water Extract. Other samples prepared

from a similar hydrolyzed rubber gave even more striking results.

Table VII—Effect of Adding Alcohol Extracts to Mercapto Stock

Material Added	Best Cure (125° C.)	Stiffness Index	Tensile
	Minutes		*Kg./sq. cm.*
Control	45	48	124
Ppt. I	30	57	117
Ppt. IV	30	69	144
Ppt. III	−45	45	136
Ppt. II	−45	64	136

Ppt. IV-*a*, butyl alcohol–soluble, non-crystalline residue. This sample was 7 months old when compounded and had a disagreeable, putrid odor.

Ppt. IV-*b*, same age and preparation as IV-*a*, but had no odor whatever.

Ppt. IV-*c*, same as IV-*a*, but freshly prepared.

Ppt. II-*b*, butyl alcohol–insoluble, water-soluble, non-crystalline residue.

Three per cent of these materials were used to activate mercapto stocks with the results shown in Table VIII.

Table VIII—Effect of Adding Water Extracts to Mercapto Stocks

Material Added	Best Cure (125° C.)	Stiffness Index	Tensile
	Minutes		*Kg./sq. cm.*
Control	100	54	132
Ppt. IV-*a*	45	101	200
Ppt. IV-*b*	−100	69	159
Ppt. IV-*c*	45	92	180
Ppt. II-*b*	100	58	152

In this case we have to deal with putrefaction bases, present in IV-*a*, which undoubtedly have considerable accelerating and stiffening action. The increase due to the action of putrefaction bases is represented by the difference between IV-*a* and IV-*c*. The latter is the same as IV in Table VII and activates similarly, considering the amount used. II-*b* is similar to II in Table VII.

The noteworthy fact about these materials is that, while they have the ability to activate mercaptobenzothiazole-accelerated stocks, they are practically without effect in a pure-gum mix. If this is true, then none of them is the natural accelerator, and none the cause of variability between different lots of the same type of rubber. This is further indicated by Tables III and IV, which show that the effect of heat is not to remove variability but to increase it.

It is possible however to correlate the effect of these extracted substances with that of the pure compounds tested in Table V. If we suppose that hydrolysis has been complete and the hydrolysate contains only the final splitting products, we find that these are the materials which do not accelerate alone, but do have the ability to activate accelerators—viz., the simplest amino acids and nitrogenous bases. The intermediate splitting products and more complex nitrogenous materials have a slight accelerating action in pure-gum mixes.

In summing up the chemical causes of the increased rate of cure, we may say that (1) amino acids, except the simplest

ones, are without effect in pure-gum cures; (2) amines and nitrogen bases activate accelerated stocks, particularly mercaptobenzothiazole; (3) alkaloids exert some accelerating and activating influence. The writers believe that all three types of compounds are present in rubber, their presence having been indicated in the water extract of heated rubber, and that they are the chemical cause of the peculiarities of heated rubber.

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Preparation of Butadiene[1]

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OF THE numerous methods available for the preparation of butadiene in the laboratory, those described by Thiele[2] and by Ostromuislenskii[3] are probably the most convenient. Both, however, suffer from the disadvantages which usually characterize operations at comparatively high temperatures; the exact conditions are difficult to find, the process is long and tedious, and finally involves the separation of the required material from a complex mixture.

It has long been known that butadiene occurs in the various products obtained when oils are heated to a high temperature. Caventou[4] first isolated butadiene in the form of its tetrabromide from illuminating gas, and Armstrong and Miller[5] definitely established the presence of butadiene in the liquid obtained by compressing oil gas. The work of numerous later investigators has confirmed their results and has shown that the more drastic the heat treatment to which the oil is submitted the greater is the tendency for butadiene to be formed. For this reason vapor-phase cracking of petroleum, which is carried out at a much higher temperature than liquid-phase cracking, yields products specially rich in butadiene. Indeed, a patent[6] for the preparation of butadiene and isoprene by the pyrolysis of petroleum oils at about 700° C., particularly

[1] Received November 21, 1927.

[2] *Ann.*, **308**, 337 (1899).

[3] *J. Russ. Phys.-Chem. Soc.*, **47**, 1494 (1915).

[4] *Ber.*, **6**, 70 (1873).

[5] *J. Chem. Soc. (London)*, **49**, 80 (1886).

[6] Engler and Staudinger, D. R. P. 265,172 (1912).

under reduced pressure, has actually been taken out. It was therefore surprising to note the opinion expressed by Brooks[7] that the isolation of butadiene from the low fractions of the liquid obtained by compressing oil gas or Pintsch gas was particularly due to the skill of the chemists, since this material might well be expected to be comparatively rich in the more volatile diolefins. In fact, a reinvestigation of this material has shown it to be a convenient and inexpensive source of butadiene, which can be readily isolated from it in the form of its tetrabromides. Owing to the cheapness of the material and the simplicity of the method of separation, it is an easy matter to prepare as large a quantity of the tetrabromides as may be desired.

Preparation of Butadiene Tetrabromide

"Railway hydrocarbon," the liquid produced during the preparation of oil gas, was distilled from a copper can in 2-gallon (9.1-liter) batches, through a 6-foot (1.8-meter) column, packed with metal rings and attached to a Liebig's condenser. The uncondensed vapors from the receiver were led into bromine (250 cc.) which was initially mixed with ice. The evolution of gas commenced long before any condensable distillate came over and was practically complete when the stillhead temperature reached 60–70° C. Decoloration of the bromine took place rapidly. Considerable heat was evolved; judicious cooling was employed, but towards the end of the experiment the reaction mixture was allowed to become sufficiently warm to prevent the solidification of the butadiene tetrabromide. To avoid loss of butadiene the bromine taken represented a slight excess. When evolution of gas had ceased, the excess of bromine was destroyed by sulfur dioxide and the bromides were washed twice with hot water. After separation of the water, the product was cooled in ice, when the whole set to a semi-solid mass. As much of the liquid as possible was then separated at the pump, the residual solid was washed with a small quantity of petroleum ether (60–80° C.) and finally crystallized from the same solvent. The solid butadiene tetrabromide separated in small, glistening, colorless plates melting, after a second recrystallization, at 117° C. The yield from 2 gallons (9.1 liters) of starting material was 200 to 210 grams; a further small crop separated from the liquid bromides and petroleum ether mother liquors on standing.

The liquid bromides were freed from solid tetrabromide as completely as possible and fractionated under reduced pressure. The fraction boiling above 150° C. at 42 mm. deposited on cooling a further crop of the solid tetrabromide (about 12 grams); this was removed and the residue refractionated. The fraction boiling at 169° C. and 30 mm. appeared to be mainly liquid tetrabromide but still contained some of the solid isomer, which again separated on cooling.

[7] "Non-Benzenoid Hydrocarbons," p. 216.

The yield was about 80 grams. When treated with zinc dust and alcohol in the manner described by Thiele,[2] it gave a colorless gas which, on passing into bromine, yielded a further quantity of the solid tetrabromide.

Further quantities of both liquid and solid tetrabromides were obtained by distilling the low-boiling hydrocarbons which collected in the receiver when the starting material was distilled. Eight gallons (36 liters) of the railway hydrocarbon gave a little over a liter of these hydrocarbons, from which about 200 grams of the crude solid tetrabromide and 145 grams of the liquid tetrabromides were obtained.

Besides butadiene tetrabromide, about 500 grams of bromides boiling from 65° to 150° C. and 42 mm. were obtained. These probably consisted mainly of isobutylene dibromide and were not further treated.

Using the method described, it is possible to distil four 2-gallon (9.1-liter) batches in one day and thus produce about 800 grams of the solid tetrabromide. Redistillation of the condensate and fractionation of the combined liquid bromides takes another day and produces a further 250 grams of the solid and 560 grams of the liquid tetrabromide.

Preparation of Pure Butadiene

Pure butadiene can be readily and conveniently prepared from the solid tetrabromide by the method described by Thiele.[2] For most purposes the once-crystallized material is pure enough. Butadiene prepared from the liquid tetrabromides is probably contaminated with traces of high-boiling olefins.

It is interesting to note that, in spite of its high boiling point, the solid tetrabromide has an appreciable vapor pressure at ordinary temperature. Hence loss by volatilization must be guarded against in attempting to dry the material in a steam oven, particularly as the vapor is lachrymatory.

Attempt to Isolate Isoprene

An attempt to isolate isoprene from the low-boiling hydrocarbons in the form of β-methyl-β,δ-dichlorobutane[3] led to the formation of a small quantity of liquid dichloride of indefinite boiling range, which was not further investigated.

[3] Ostromuislenskii, *J. Russ. Phys.-Chem. Soc.*, **47**, 1983 (1915).

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Direct Determination of Rubber in Soft Vulcanized Rubber[1]

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A modification of the Wijs method is shown to be suitable for determining the rubber content of vulcanized rubber.

A procedure for the direct determination of sulfur combined with rubber is outlined.

The effect of compounding ingredients is shown.

Results of analyses of four reclaimed rubbers by the proposed and difference methods are given for comparison.

THE need for a rapid direct method for determining rubber in vulcanized rubber has long been recognized. In a previous paper[2] a direct method was given for determining the hydrocarbon content of crude rubber and gutta-percha based upon the additive reaction of iodochloride (Wijs solution) with their hydrocarbons. It is the purpose of the present paper to describe a modification of this method for determining the rubber content of soft vulcanized rubbers. Although several direct methods[3] are described in the literature, none of them have been found entirely satisfactory. A widely used method for determining the rubber content in vulcanized rubbers is that recommended by the Committee on Methods of Analysis of the Division of Rubber

[1] Received October 25, 1927.

[2] Kemp, *Ind. Eng. Chem.*, **19**, 531 (1927).

[3] Alexander, *Gummi-Ztg.*, **18**, 789 (1904); Axelrod, *J. Soc. Chem. Ind.*, **26**, 1058 (1907); Lewis and McAdams, *J. Ind. Eng. Chem.*, **12**, 673 (1920).

Chemistry of the AMERICAN CHEMICAL SOCIETY.[4] This method is a complicated one and consists in determining the non-rubber constituents and taking rubber by difference. As mentioned in the committee report, the method is inaccurate in the presence of decomposable inorganic constituents, cellulose, or high percentages of mineral rubber. The principal objection to it, however, is the time required for performing the analysis.

Outline of Proposed Method

Briefly, the method consists in extraction with acetone of resins, free sulfur, oils, waxes, organic accelerators, age resistors, part of the mineral rubber, etc., followed by further removal of a portion of the mineral rubber with chloroform. A sample of the extracted residue is then dissolved in tetrachloroethane and the hydrocarbon present in the unsaturated state determined by the modified Wijs method.[2,5]

In order to determine the amount of hydrocarbon saturated with sulfur, a direct determination of sulfur combined with rubber is made on another portion of the extracted sample. The sum of the hydrocarbons in the unsaturated and combined states is then used to calculate the rubber content of the original sample.

Experimental Procedure

The acetone and chloroform extractions are carried out on 2-gram samples according to standard procedure.[4] The chloroform is removed by heating in a vacuum oven at 70° C. to constant weight. An alcoholic alkali extraction is also conducted on one of the extracted samples to detect the presence of factice, for which, if present, correction is made as shown later. An accurately weighed portion of the acetone- and chloroform-extracted residue containing 0.07 to 0.10 gram of rubber which has been cut into very small pieces (20 mesh) is completely dispersed by refluxing in 50 cc. of tetrachloroethane for from 3 to 5 hours. (Eastman's technical grade fractionated between 146.5° and 147.5° C. (cor.) using a 24-inch Young column. After refluxing 5 hours 50 cc. should not liberate iodine from potassium iodide equivalent to more than 0.5 cc. of 0.1 *N* sodium thiosulfate.) For this purpose an Underwriter's flask[5] with glass condenser similar in design to the Underwriter's block tin condenser[6] is used. It has been found that careful heating is essential to obtain concordant results. This is accomplished by the use of an oil bath kept at 160–170° C. The flask containing the sample is so arranged that the level of the solvent is slightly above the level of the oil in the bath. "Scorching" of the sample is thus prevented. A blank determination is performed at the same time.

After dispersion is complete, the flask is removed from the

[4] *Ind. Eng. Chem.*, **16**, 397 (1924).
[5] Fisher, *India Rubber World*, **76**, 78 (1927).
[6] L. Weber, "Chemistry of Rubber Manufacture," p. 111.

bath, allowed to cool, and the contents diluted with 25 cc. of carbon bisulfide (C. P. grade, purified by allowing to stand in contact with solid potassium hydroxide for 48 hours and finally distilled over same). Twenty-five cubic centimeters of 0.2 *N* Wijs solution are then added from a pipet, the flask is covered and immediately placed in ice water, and the reaction is allowed to proceed for 2 hours in diffused light under ordinary laboratory conditions. At the end of this period 25 cc. of 15 per cent potassium iodide solution and 50 cc. of distilled water are added. The liberated iodine is then titrated with 0.1 *N* sodium thiosulfate.[7] Before the brownish color of iodine has disappeared from the aqueous layer, 5 cc. of a 5 per cent soluble starch solution are added as an indicator. At this point the flask must be shaken vigorously to remove last traces of iodine from the solvent layer. Also care must be taken to allow dark suspended materials to settle after each shaking; otherwise, their coloration in suspension might obscure the end point. After the end point has been reached the aqueous layer should be colorless and remain so after shaking and standing. The difference between the blank and sample titration is used to calculate the iodine number in the usual manner.

Procedure for Sulfur Combined with Rubber

A 0.5-gram sample of the acetone- and chloroform-extracted residue is refluxed in 50 cc. of tetrachloroethane under the identical conditions mentioned above. After dispersion is complete, the contents of the flask are transferred to a 250-cc. volumetric flask with the aid of hot carbon tetrachloride. After the contents of the volumetric flask have cooled to 25° C., the solution is made up to the mark with carbon tetrachloride, the contents shaken thoroughly and the solids separated by centrifugation or allowed to settle overnight. One-hundred cubic centimeters of the upper portion of the solution are then pipetted and transferred to a 125-cc. porcelain crucible. The solvent is evaporated on a steam bath and the sulfur in the residue determined according to the method of Waters and Tuttle.[4,8]

Calculation of Results

The theoretical iodine value for pure rubber hydrocarbon based on one double bond for every C_5H_8 group is 372.8; hence, the percentage of unsaturated hydrocarbon in the extracted residue is given by the ratio of the iodine value obtained for the sample to the theoretical iodine value. The hydrocarbon which is combined with sulfur is given by multiplying the per cent combined sulfur in the extracted residue by 2.13, which is the ratio of hydrocarbon to sulfur in C_5H_8S. The hydrocarbon in the original sample is obtained by multiplying the hydrocarbon content found in the extracted residue by the difference between 100 and the combined per-

[7] Popoff and Whitman, *J. Am. Chem. Soc.*, **47**, 2259 (1925).

[8] *Bur. Standards, Sci. Paper* **174** (1911).

centages of acetone and chloroform extracts. For example:

$$\text{Per cent hydrocarbon in original sample} = \frac{\left(\frac{100\,A}{372.8} + 2.13\,B\right)(100 - C)}{100}$$

A = iodine value of acetone- and chloroform-extracted residue
B = Per cent sulfur combined with rubber in acetone- and chloroform-extracted residue
C = percentage of acetone and chloroform extracts

Effect of Non-Rubber Constituents

Any method proposed for determining rubber in commercial rubber articles must take into account the large number of organic and inorganic compounding ingredients which may be present, as some of these materials may seriously affect the accuracy of a method. The presence of an unsaturated material other than rubber which will absorb iodochloride will obviously cause the results to be high. Resins, oils, waxes, accelerators, age resistors, etc., some of which have high iodine values, are removed by acetone and chloroform. Carbon black, glue, cellulose, and inorganic compounding ingredients do not absorb appreciable iodochloride. Mineral rubber is only partly extracted by acetone and chloroform, leaving a residue soluble in tetrachloroethane having a degree of unsaturation which will cause only a small error even when present in large quantities. Factice, on the other hand, is almost completely soluble in tetrachloroethane and has a high degree of unsaturation and a high combined-sulfur content, which introduce an error in the result for which correction must be made.

The effect of carbon black, glue, cellulose, and a variety of inorganic compounding ingredients upon the results was tested by applying the foregoing method to 0.1-gram samples of these materials. The inorganic compounding ingredients tested were litharge, magnesium oxide, lithopone, zinc oxide, whiting, lime, Dixie clay, and talc. The results showed that the absorption of iodochloride by any of these materials except cellulose is practically nil. In the case of a sample of extracted absorbent cotton the iodine value was found to be 7.8; therefore, 5 per cent of cellulose in a compound would be equivalent to only 0.1 per cent rubber hydrocarbon. The presence of cellulose as well as the other compounding materials mentioned above may therefore be neglected in this method of analysis.

Weber[9] places the amount of mineral rubber insoluble in acetone and chloroform after vulcanization at 45 per cent. The iodine value of a sample of mineral rubber as determined by the method outlined above was 65.7. In a compound containing 10 per cent mineral rubber the insoluble portion, if equally unsaturated, would cause an error of less than 1 per cent in the hydrocarbon content on the basis of Weber's

[9] *Op. cit.*, p. 216.

figure of 45 per cent unextracted material. In the case of compound II in Table II it was found that 70 per cent of the mineral rubber added was extracted by the acetone and chloroform. In general, the effect of ordinary amounts of mineral rubber is small, though perhaps not entirely negligible in extreme cases.

Table I—Analysis of Factice

	Brown	White
	Per cent	*Per cent*
Acetone extract	13.8	4.4
Chloroform extract	0.10	0.03
Combined sulfur (extracted residue)	9.65	7.84
Iodine value (extracted residue)	115.0	90.0

Table II—Composition of Rubber Compounds

Constituent	I	II	III	IV	V
Smoked sheet	92.5	83.3	80	80	60.0
Sulfur	7.5	3.4	3	3	2.4
Diphenylguanidine			2	2	
Tetramethylthiurammonosulfide		0.8			1.0
Mineral rubber		8.3			4.0
Mineral oil					0.3
Stearic acid					0.3
Factice (brown)			10		
Factice (white)				10	
Zinc oxide		4.2	5	5	12.0
Carbon black					20.0
Total	100.0	100.0	100	100	100.0

Table III—Average Analyses of Compounds in Table II

	I	II	III	IV	V
Acetone extract	8.35	8.89	7.55	7.32	7.45
Chloroform extract		2.64	0.92	1.50	0.75
Alcoholic potash extract			5.28	6.54	
Iodine value of extracted residue	334.8	317.8	310.5	301.3	216.7
Sulfur combined with rubber in extracted residue	2.37	1.28	2.84	2.19	1.54
Rubber hydrocarbon:					
Found	86.9	77.9	77.0	72.5	56.2
Calculated[a]	86.0	77.4	74.4	74.4	55.8
Difference	+0.9	+0.5	+2.6	−1.9	+0.4

[a] In calculating the hydrocarbon content 93.0 per cent was used as the hydrocarbon content of first-quality smoked sheets. This is in accordance with Whitby, "Plantation Rubber," p. 60 (1920), who gives the hydrocarbon content of first-quality plantation rubbers as varying between 92.1 and 94.6 per cent. DeVries, "Estate Rubber," pp. 14 and 601 (1920), states that the hydrocarbon content of first-quality plantation rubber varies between 92 and 94 per cent. Results obtained by the modified Wijs method agree with the figures mentioned above.

To illustrate the need for correcting for factice, analyses of samples of the brown and white varieties are given in Table I. On the basis of these analyses 1 per cent of brown factice in a rubber compound is equivalent to 0.45 per cent of rubber hydrocarbon. In a similar manner 1 per cent of white factice is equivalent to 0.40 per cent of hydrocarbon.

In analyzing rubber compounds containing factice, it would seem at first that the analyses should be carried out on the alcoholic potash–extracted sample. It has been found, however, that in most cases this treatment, even after thorough removal of moisture and free alkali, changes the rubber to a condition such that it is insoluble in the tetrachloroethane. Furthermore, as shown in Table III, the alcoholic alkali extraction process removes only about 60 per cent of the factice added. When the alcoholic potash extract exceeds 1 per

cent, indicating the presence of factice, the rubber hydrocarbon content is calculated in accordance with the formula already given, except that the value of C for total extracts should include the alcoholic potash extract.

Results of Analyses

Several compounds the compositions of which are given in Table II were analyzed by the method outlined. The results of the analyses are given in Table III. These compounds were chosen for the purpose of showing the effects of various compounding ingredients, and therefore do not conform to the best rubber-compounding practice. Because of their indefinite rubber content the analyses of reclaimed rubbers are given in a separate part of the paper.

Table IV—Analyses of Reclaims by Manufacturers' Shortened Difference Methods[a]

	Boot and Shoe I	Black Tire II	Mixtures—Boot and Shoe and Tire III	Mixtures—Boot and Shoe and Tire IV
	Per cent	*Per cent*	*Per cent*	*Per cent*
Acetone extract (unvulc.)	10.8	11.5	10.0	13.0
Chloroform extract (vulc.)	...	...	...	...
Alcoholic potash extract	0.65	0.49	...	...
Total sulfur (unvulc.)	5.75	2.51	3.50	3.50
Ash (unvulc.)	47.7	25.4	25.0	24.0
Total	64.9	39.9	38.5	40.5
Rubber by difference (unvulc)	35.1	60.1	61.5	59.5

[a] These analyses were furnished by the manufacturers of the products The samples were cured with 2 per cent sulfur preparatory to analysis, according to information furnished.

Table V—Average Analyses of Reclaims[a] by the Standard Difference Method[b]

	I	II	III	IV
Organic acetone extract (vulc.)	10.73	10.65	10.31	12.40
Chloroform extract (vulc.)	1.62	1.55	1.57	1.67
Alcoholic potash extract (vulc.)	0.65	0.49	0.50	0.50
Total sulfur (net) (vulc.)	6.27	5.03	4.50	4.62
Ash (vulc.)	44.7	30.7	25.7	26.8
Carbon (vulc.)	2.54	5.49	2.13	1.81
Cellulose (vulc.)	4.51	1.47	1.48	3.96
Total (vulc.)	71.02	55.38	46.19	51.76
Rubber hydrocarbon by difference:				
Vulcanized	28.98	44.62	53.81	48.24
Unvulcanized	29.9	46.0	55.5	49.8

[a] Reclaims were cured with 3 per cent sulfur before analyzing to render insoluble in chloroform that portion of the rubber which had been rendered soluble by the reclaiming process. Results corrected for cellulose and carbon.

Table VI—Average Analyses of Reclaims by the Proposed Method[a]

	I	II	III	IV
Acetone extract	11.13	12.69	11.52	13.30
Iodine value of acetone extracted residue	106.4	173.0	206.5	185.3
Sulfur combined with rubber in acetone extracted residue	1.09	2.39	2.75	2.51
Rubber hydrocarbon found	27.4	45.0	54.2	47.7

[a] Samples unvulcanized and chloroform extraction omitted.

Analysis of Reclaimed Rubber

As reclaimed rubber is present in many commercial rubber compositions, the estimation of its rubber content is a matter of importance. Since a portion of the rubber in uncured reclaims is removed by chloroform extraction, it is necessary

either to omit this process or to cure the reclaim previous to analysis. Tables IV, V, and VI give the results of analyses of four commercial reclaims by the manufacturers' shortened difference methods, standard difference method, and the proposed direct method, respectively. The results in Table IV are evidently not corrected for carbon black or cellulose, both of which are present. Unextracted mineral rubber and decomposable inorganic compounding ingredients also would tend to make the rubber content high in this method. The sulfur remaining in the ash, however, would reduce the rubber content, thus compensating in part for the other additive errors.

Discussion

In developing this method much depended upon the selection of a suitable solvent. Of the many solvents proposed for vulcanized rubber, tetrachloroethane was found to be the best. Pentachloroethane was also tried but was found to be unsatisfactory, especially with compounds containing reclaimed rubber. In this case the rubber appeared to disperse completely, but on continued heating for a short time it separated out as a flocculent mass. It was found that tetrachloroethane supplied from different sources after very careful fractionation behaved differently in the blank determinations. Some of the samples, after refluxing in contact with air liberated variable amounts of iodine from potassium iodide. However, the grade of solvent specified in the procedure has been found to give satisfactory results.

It appears that the rate of dispersion of soft vulcanized rubber in tetrachloroethane depends to a large degree upon the state of vulcanization. Pure vulcanized rubbers with low vulcanization coefficients disperse rapidly, but reclaims with high coefficients, slowly. It has been found, for example, that rubber compositions free from reclaim will disperse in 1 to 3 hours, while compositions containing high percentages of reclaim such as some wire insulations may require 5 hours. Some reclaimed rubbers also require this longer period for dispersion.

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"Normal Aging" of Compounded Rubber[1,2]

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Nine compounds were chosen for an investigation of "normal aging" under various conditions and after different times of storage. The report is divided into three parts: (I) aging of cured test slabs stored under different atmospheric conditions, including wet and dry; (II) aging of rubber under strain; (III) comparative aging of cured and uncured rubber. Tables and curve sheets selected from a large mass of data are given to illustrate how these nine rubber compounds age.

THE aging of rubber products is the net resultant of chemical reactions and changes of a physico-chemical nature.

It has long been recognized that conditions of storage have an important influence on the normal aging of rubber products. Rubber products stored in a warm place deteriorate more rapidly than when stored in a cold place, and it probably was recognition of this fact that led to the development of the Geer[3] accelerated-aging test, which accelerates aging solely by increasing the temperature during storage. Oxygen is also an important factor in the aging of rubber products. In normal storage the oxygen concentration varies very little, and depends only on the barometric pressure. In specific cases, such as inner tubes, the oxygen concentra-

[1] Received November 23, 1927.

[2] Presented by Mr. Depew in partial fulfilment of the requirements for the degree of doctor of philosophy from Columbia University.

[3] Geer and Evans, *India Rubber J.*, **61**, 1163 (1921).

tion may vary considerably according to the air pressure in the tube. Recognition of this as well as the temperature factor led to the development of the Bierer-Davis[4] oxygen-bomb method of accelerated aging.

Aging is also affected by moisture. Stringfield[5] has pointed out the importance of humidity in testing, Conover[6] and one of the authors have made recommendations for controlling laboratory humidity, and Stevens[7] has shown that moisture improves the resistance to aging of certain stocks.

It is well known that conditions of strain influence the life of vulcanized rubber and that light accentuates the deterioration. It seems probable that fluctuations in temperature and humidity, including freezing temperatures, may also affect the life of rubber products in storage. Consequently, there is no such thing as normal storage and statements giving the number of months' normal storage equivalent to one day's accelerated aging are meaningless unless the conditions of normal storage are carefully prescribed.

Consider the Geer test in its relation to "normal aging." The accelerated test is conducted at 70° C. If the "normal aging" is conducted at 20° C., the temperature difference is 50° C., enough to accelerate the aging 172 times on a basis of an increase of 2.8 times for each 10° C. On the other hand, with the storage temperature at 30° C. the acceleration of aging would be 61 times. In the former case an investigator would report one day of accelerated aging as approximately equivalent to 6 months' storage; in the latter, one day would be equivalent to 2 months' storage.

From these considerations one can readily understand why investigators are unable to agree on the quantitative relation between accelerated and "normal" aging tests. Inasmuch as conditions of accelerated aging can be controlled more easily than conditions of "normal aging" during the shorter time of test, accelerated tests can probably be duplicated more easily than natural aging tests. This alone justifies considerable interest in accelerated aging tests.

As a first step in the understanding of accelerated aging tests, a program was outlined to obtain information about "normal aging." Nine compounds were chosen (Table I) and the aging was determined after various conditions and times of storage.

I—Aging of Cured Test Slabs Stored under Different Atmospheric Conditions

The test slabs were 5 by 6 by 0.15 inch (12.7 by 15.2 by 0.38 cm.) in size and were suspended from a steel rod by paper clips in boxes maintained at the desired atmospheric conditions as follows:

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[4] Bierer and Davis, IND. ENG. CHEM., **16**, 711 (1924); **17**, 860 (1925).
[5] *Ibid.*, **17**, 833 (1925).
[6] Conover and Depew, *Proc. Am. Soc. Testing Materials*, **27**, 493 (1927).
[7] *J. Soc. Chem. Ind.*, **39**, 251T (1920).

(1) Outdoors on the roof of the laboratory in an open box protected from direct light by shutters. (Figure 1) The temperature varied from below zero (−17.8° C.) to over 100° F. (37.8° C.). The relative humidity varied from 40 per cent to 100 per cent. The average figures for the 4 years were 48° F. (8.9° C.) and 72 per cent relative humidity.

(2) Indoors in a duplicate open box in a dark room. The temperature varied from about 50° F. (10° C.) to 85° F. (29.4° C.) and the relative humidity varied from 25 per cent to 100 per cent. In the winter the average humidity was lower indoors than out, and in the summer the average indoor humidity was unusually high, owing to an air-washing installation in the building.

(3) Indoors in a tight box lined with sheet zinc. Air, dried by passing through sulfuric acid, was passed through the box continuously.

(4) Indoors in a tight box lined with sheet zinc. Air, humidified by bubbling through moist glass wool, was passed through the box continuously.

The effectiveness of the drying and humidification was demonstrated qualitatively by the fact that the iron clips holding the samples corroded through in the wet box in a short time, whereas there was practically no corrosion in the dry box.

Results and Discussion of Data—(1) The stress-strain curves made for slabs that had received 4 years of normal aging show that in most cases the rubber stored in the wet box has the "softest" stress-strain curve and rubber stored in the dry box has the "stiffest" stress-strain curve. (Curves 1 to 21)

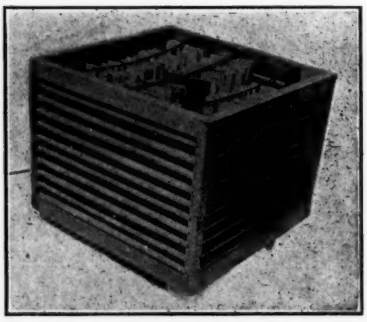


Figure 1—Arrangement of Test Slabs in the Open Storage Boxes; the Slabs Being Supported from Metal Rods by Clips. They Are Protected from Direct Light by Open Shutters and a Wooden Top

(2) Overcured rubber deteriorates faster in a dry than in a wet atmosphere; the reverse is the case for undercured rubber. (Curves 1 to 21 and 22 to 24) Stevens[7] showed that moisture improved the aging resistance of his stock. If the rubber compounds with which he experimented were tightly cured—and this seems probable—his results are in complete harmony with those of the present writers.

(3) The improvement in aging of the overcures in a wet atmosphere and of the undercures in a dry atmosphere is somewhat masked on the curve sheets by the superior aging that is shown by some of the compounds in the open box outdoors.

A possible explanation of this surprising fact is based on

Table I—Compounds Investigated
(Figures in parts by weight)

Compound	Pale Crepe	Sulfur	Hexamethylenetetramine	XX Red Zinc Oxide	Clay	Paraffin	Triphenylguanidine	Magnesia	Black Label Kadox
A—Typical white tread stock	920	55	6	1260	...	..	..	..	..
B—Lower sulfur white tread stock	920	37	13	1260	...	..	..	..	..
C—Gum compound with zinc oxide for activation	920	55	6	28	...	..	..	..	..
D—"Pure gum" compound	920	55	..	..	...	..	..	..	..
E—Clay compound	920	55	6	..	597	..	..	..	..
F—Compound containing paraffin	920	55	6	1260	...	5	..	..	..
G—Compound with T. P. G. substituted for hexa	920	55	..	1260	...	..	12	..	..
H—Inorganic accelerated compound	920	55	..	1148	...	..	..	64	..
I—Compound containing a fine-particle-size zinc oxide	920	37	6	..	...	..	..	..	1035

1260 parts of zinc oxide by weight compared with 920 parts of rubber calculates as 22.5 volumes of pigment to 100 volumes of rubber.

the belief of many technologists that rubber ages better in service than on the shelf. Changes in humidity with corresponding changes in moisture content, and therefore volume, and changes in temperature with resultant contraction and expansion, might work the rubber sufficiently to improve its resistance to aging. It is planned to check this theory by experimental tests. In the meantime it will serve until some better explanation is offered.

(4) The 60-minute cure of the clay compound (E) aged much better in the dry box than in the wet box. (Curves 13 and 14) Visual observation would have led to the opposite conclusion, for the surface of the slab aged in the dry box had hardened and could easily be cracked by bending. (Figure 2) Although the surface of the test slab in the dry box was poorer than that in the wet box, the center of the slab in the dry box appeared to be better than that in the wet box.

The fact that slabs of rubber only $^1/_8$ inch (3 mm.) thick show a marked difference in aging on the surface and in the interior is especially interesting. The stress-strain curves of these test slabs are concave to the elongation axis. This is due to minute failures in the test piece (surface breaks) as it stretches. At first the surface carries most of the stress, but when the surface cracks the soft center has to carry the load. This concave curve can be noted in fiber compounds when the rubber-fiber bond breaks down, and in heavily loaded stocks when the rubber-pigment bond is breaking down.

The composition of the clay stock may not have been such as to give the best results obtainable with such a stock; therefore, no direct pigment comparison can be made or is intended. The stock aged poorly, doing best in the outdoors box.

The degree of surface cracking depends on the state of cure, the higher cures showing the more severe cracking. All the cures of compound D, and the two highest cures of compound C in the dry box cracked on bending, but these pieces were brittle throughout their thickness and not only on the surface.

Table II—Effect of One Month's Drying at Room Temperature on Stress-Strain Properties of Test Slabs Aged in a Wet Atmosphere
(Compound A)

Time of Cure at 141.5° C.	Tensile Strength		Elong.	Load at Elongation of:					
				150%		300%		450%	
Min.	*Kg./sq. cm.*	*Lbs./sq. in.*	*%*	*Kg./sq. cm.*	*Lbs./sq. in.*	*Kg./sq. cm.*	*Lbs./sq. in.*	*Kg./sq. cm.*	*Lbs./sq. in.*
AGED 4 YEARS AND 3 MONTHS IN WET BOX									
60	144	2055	545	23	320	53	750	105	1500
100	124	1765	475	32	455	66	945	119	1690
110	126	1795	480	32	460	62	875	118	1680
130	95	1355	385	36	505	67	945	Break	
AGED 4 YEARS AND 2 MONTHS IN WET BOX AND THEN 1 MONTH IN DRY BOX									
60	163	2320	540	28	395	65	920	121	1715
100	147	2095	475	39	555	83	1175	140	1985
110	122	1730	415	40	575	84	1195	Break	
130	113	1605	370	49	700	94	1330	Break	

(5) Slabs that have been aged for 4 years and 2 months in a wet box and then dried for 1 month by exposure to a dry atmosphere have a higher tensile strength by 300 to 400 pounds per square inch (21 to 28 kg. per sq. cm.) than slabs that have been kept continually in a wet atmosphere. Strangely enough, this improvement seems to be independent of state of cure. (Table II)

(6) During the first year's storage the change in weight in the wet box is no doubt largely a measure of the change in moisture content. In all cases, except the "pure gum" compound, where the results were irregular, the slabs in the wet box gained the most in weight. The samples in the dry box actually lost weight in a number of cases. (Table III)

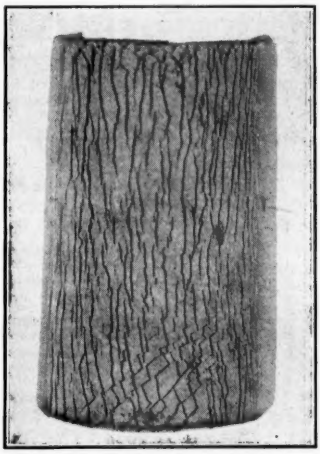


Figure 2—Strained Test Slab of Clay Compound (60-Minute Cure) after 4 Years in Dry Atmosphere

After the first year the rate of increase in weight in the wet box is less. It seems probable that the moisture content has reached equilibrium and that further changes in weight in both boxes are due largely to oxidation. The time required to come to equilibrium would probably have been greatly reduced if the dry or moist air had blown rapidly over the test slabs. In the indoor and outdoor boxes changes in temperature and humidity caused the weights to change irregularly.

Those data in Table III dealing with the change in weight of the slabs in the wet and dry boxes have been recalculated (Table IV) to show the difference in the increase in weight in the wet and dry atmospheres.

If the compounds oxidize at the same rate, the difference in weight increase should remain constant after the first year. If the test piece oxidizes more rapidly in the dry box, the difference in weight increase should diminish. The data show, in the case of compound A, that the curves other than the overcure oxidize at about the same rate in both the wet and dry atmospheres but the overcure oxidizes less in the wet atmosphere.

Since the undercure of compound A, for example, oxidized at about the same rate in the wet and dry atmospheres, but deteriorated in physical properties to a greater extent in the wet atmosphere as shown by tensile strength tests, it must be concluded that oxidation alone will not explain the aging of rubber. Without these data one might think that

Table III—Change in Weight Calculated on a Basis of 100 Per Cent Rubber

(Figures in per cent)

Comp.	Time of Cure	Aged 4 Months				Aged 12 Months				Aged 24 Months				Aged 48 Months			
		Out-door	Indoor	Dry box	Wet box	Out-door	Indoor	Dry box	Wet box	Out-door	Indoor	Dry box	Wet box	Out-door	Indoor	Dry box	Wet box
A	60	+0.29	+0.22	−0.17	+0.37	+0.49	+0.20	−0.07	+1.73	+0.78	+0.20	+0.07	+1.88	−0.27	+0.27	+0.34	+2.05
	100	+0.32	+0.22	−0.10	+0.34	+0.63	+0.32	+0.24	+1.56	+1.12	+0.66	+0.54	+1.88	+0.59	+1.39	+0.98	+2.34
	110	+0.34	+0.24	−0.05	+0.41	+0.63	+0.39	+0.34	+1.83	+1.17	+0.81	+0.68	+2.02	+0.61	+1.46	+1.12	+2.54
	130	+0.41	+0.46	+0.07	+0.41	+0.90	+0.73	+0.59	+2.00	+1.78	+1.20	+1.10	+2.15	+1.46	+1.93	+2.09	+3.00
B	50	+0.41	+0.12	−0.29	+0.41	+0.44	+0.07	−0.29	+1.95	+0.44	+0.02	−0.10	+2.32	−0.12	+0.02	+0.22	+2.37
	80	+0.22	+0.02	+0.07	+0.46	+0.34	−0.07	−0.19	+2.57	+0.56	+0.07	+0.07	+2.20	−0.05	+0.48	+0.56	+2.52
	90	+0.22	+0.15	−0.24	+0.51	+0.29	+0.10	+0.07	+2.69	+0.46	+0.31	+0.82	+2.30	+0.22	+0.82	+1.62	+2.76
	120	+0.31	+0.31	+0.34	+0.65	+0.61	+0.65	+1.21	+3.00	+1.40	+1.45	+2.08	+2.93	+1.31	+2.45	+3.61	+3.87
C	50	+0.27	+0.15	−0.24	+0.31	+0.31	+0.15	−0.21	+1.49	+0.52	+0.27	−0.10	+1.52	0.0	+0.43	+0.24	+1.80
	90	+0.27	+0.24	0.0	+0.46	+0.58	+0.57	+0.37	+1.92	+1.71	+1.16	+0.72	+2.06	+2.11	+1.86	+1.34	+2.70
	100	+0.21	+0.28	−0.04	+0.60	+0.71	+0.72	+0.37	+2.37	+1.99	+1.37	+0.97	+2.43	+2.56	+2.18	+2.01	+3.05
	120	+0.57	+0.62	+0.09	+0.98	+1.71	+1.46	+0.63	+3.09	+2.98	+2.38	+1.59	+3.23	+4.12	+4.27	+3.52	+3.94
D	180	+0.37	+0.30	−0.05	+0.39	+0.48	+0.23	+0.05	+1.68	+0.74	+0.21	+0.14	+1.74	+0.90	+0.41	+0.62	+2.40
	240	+0.41	+0.30	+0.05	+0.43	+0.53	+0.30	+0.23	+1.90	+0.85	+0.42	+0.98	+1.79	+2.11	+1.18	+3.89	+2.66
	270	+0.39	+0.23	0.0	+0.39	+0.62	+0.32	+0.19	+2.16	+1.27	+0.84	+1.22	+2.27	+2.83	+2.32	....	+7.86
	330	+0.53	+0.33	0.0	+0.53	+1.28	+0.59	+0.23	+2.66	+3.33	+1.78	+2.06	+3.30	+4.85	+7.31	+3.92	+8.89
E	60	+0.29	+0.15	−0.12	+0.46	+0.74	+0.29	+0.19	+2.37	+1.39	+0.82	+1.40	+3.15	+1.81	+2.26	+2.63	+6.12
	90	+0.38	+0.17	−0.10	+0.58	+1.01	+0.55	+0.38	+3.11	+1.93	+1.39	+1.54	+5.47	+2.34	+3.40	+2.75	+8.74
	100	+0.38	+0.31	+0.03	+0.63	+1.11	+0.72	+0.65	+3.20	+1.95	+1.66	+2.38	+5.30	+2.29	+3.61	+3.23	+8.55
	130	+0.55	+0.53	+0.10	+0.72	+1.42	+1.23	+0.91	+3.59	+2.33	+2.98	+2.57	+6.77	+2.72	+4.00	+3.44	+8.89
F	50	+0.32	+0.15	−0.24	+0.27	+0.34	+0.12	−0.17	+1.22	+0.56	+0.12	−0.10	+1.39	+0.07	+0.15	+0.15	+1.56
	80	+0.29	+0.15	−0.15	+0.37	+0.39	+0.17	0.0	+1.46	+0.81	+0.29	+0.56	+1.59	+0.02	+0.41	+0.68	+1.80
	90	+0.29	+0.22	−0.17	+0.29	+0.46	+0.27	+0.02	+1.32	+0.95	+0.34	+0.39	+1.56	+0.54	+0.68	+0.71	+1.71
	120	+0.32	+0.32	−0.15	+0.32	+0.61	+0.49	+0.17	+1.68	+1.29	+0.93	+0.54	+1.83	+1.37	+1.58	+1.20	+2.20
G	70	+0.22	+0.05	−0.09	+0.19	+0.46	+0.41	+0.27	+1.10	+1.05	+1.05	+0.61	+1.24	+1.07	+1.73	+1.15	+1.65
	90	+0.22	+0.02	−0.12	+0.19	+0.51	+0.44	+0.51	+1.29	+1.14	+0.98	+0.98	+1.39	+1.39	+1.90	+2.00	+1.92
	100	+0.17	+0.07	+0.07	+0.22	+0.49	+0.56	+0.75	+1.29	+1.12	+1.27	+1.58	+1.49	+1.46	+2.41	+3.46	+2.21
	130	+0.32	+0.61	+0.15	+0.63	+0.90	+1.53	+1.22	+2.00	+1.83	+1.43	+2.65	+2.49	+2.26	+4.38	+4.87	+3.63
H	90	+0.38	+0.26	+0.05	+0.50	+0.79	+0.40	+0.14	+2.21	+1.33	+0.60	+0.38	+4.45	+0.55	+0.95	+0.74	+6.14
	150	+0.45	+0.43	+0.17	+0.55	+0.95	+0.74	+0.55	+2.26	+2.02	+1.07	+0.91	+4.19	+2.43	+1.83	+1.67	+6.81
	180	+0.50	+0.38	+0.29	+0.62	+1.33	+0.86	+0.83	+2.62	+2.91	+1.50	+1.40	+4.77	+3.72	+2.71	+3.07	+7.48
	210	+0.64	+0.62	+0.74	+0.76	+1.76	+1.33	+1.83	+4.17	+3.26	+2.53	+3.38	+6.59	+4.23	+4.52	+5.88	+9.60
I	30	+0.26	0.0	−0.13	+0.76	+0.22	....	....	+1.33	+0.26	....	....	+1.41	....	....	....	+1.41
	50	+0.39	+0.02	−0.20	+0.83	+0.52	....	....	+1.41	+0.76	....	....	+1.94	....	....	....	+1.74
	60	+0.43	+0.11	−0.30	+0.85	+0.72	....	....	+1.52	+1.11	....	....	+1.83	....	....	....	+2.09
	90	+0.63	+0.26	+0.15	+0.89	+1.15	....	....	+1.85	+2.13	....	+2.59	+2.44	....	....	....	+3.02

moisture in rubber influenced aging because it simultaneously influenced oxidation to a corresponding degree.

Boggs and Blake[8] have shown that the absorption of water causes rubber to swell. This swelling puts the rubber under continuous strain, which may cause it to age more rapidly from a physical viewpoint than would be expected from the data on the weight increase due to oxygen absorption; this difference in physical-chemical aging is especially large in undercured stocks, which swell to the greatest extent.

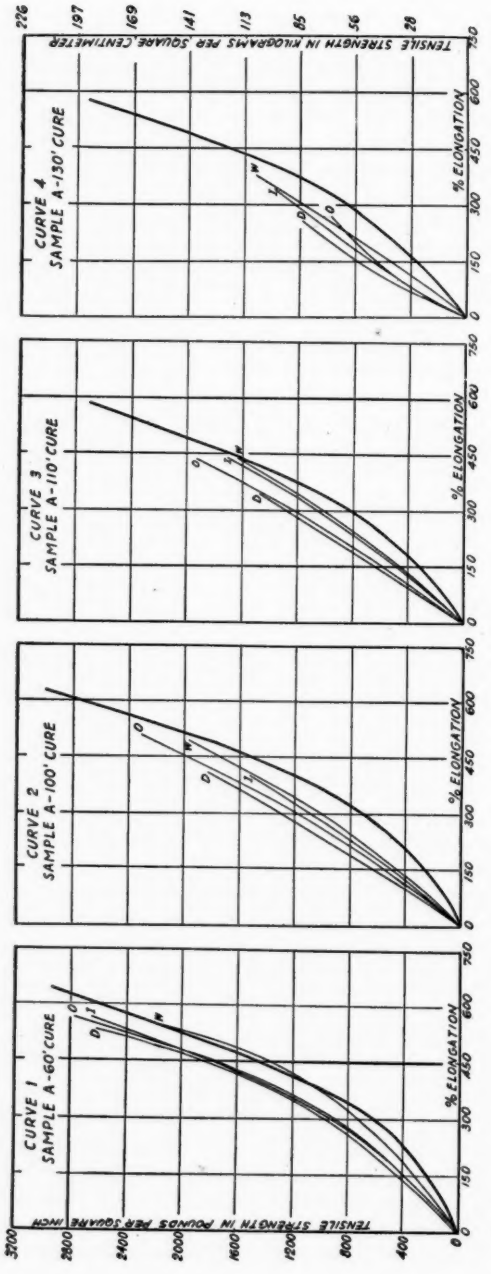
Since moisture retards the oxidation of an overcured slab, why does it not greatly reduce the oxidation of the undercured compound, where much more moisture is absorbed? The answer is probably linked closely with the structure of rubber.

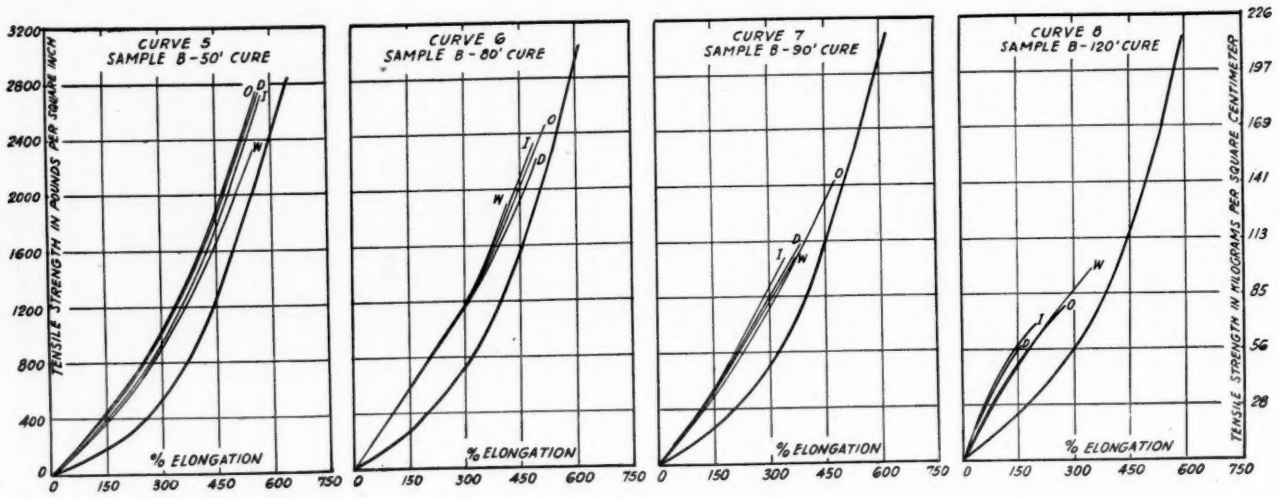
Table IV—Difference in Weight Increase in Wet and Dry Atmospheres, Calculated on a Basis of 100 Parts of Rubber
(Figures in per cent)

Comp.	Time of Cure	Time of Aging—Months						
		4	8	12	18	24	36	48
	Min.							
A	60	0.54	1.15	1.80	1.81	1.81	1.64	1.71
	100	0.44	0.86	1.32	1.39	1.34	1.22	1.36
	110	0.46	0.85	1.49	1.44	1.34	1.24	1.42
	130	0.34	0.76	1.41	1.22	1.05	0.88	0.91
B	50	0.70	1.55	2.24	2.54	2.42	2.01	2.15
	80	0.39	1.84	2.76	2.41	2.13	2.74	1.96
	90	0.75	1.70	2.62	2.09	1.48	1.07	1.14
	120	0.31	0.92	1.79	1.25	0.85	0.43	0.26
C	50	0.55	1.16	1.70	1.65	1.62	1.21	1.56
	90	0.46	0.96	1.55	1.29	1.34	1.14	1.36
	100	0.64	1.32	2.00	1.65	1.46	1.06	1.04
	120	0.89	1.79	2.46	2.01	1.64	0.70	0.42
D	180	0.44	1.18	1.63	1.75	1.60	1.29	1.78
	240	0.38	0.97	1.67	1.44	0.81	−0.87	−1.23
	270	0.39	1.27	1.97	1.71	1.02	..	..
	330	0.53	1.59	2.43	2.09	1.24	2.32	4.97
E	60	0.58	1.35	2.18	2.20	1.75	2.13	3.49
	90	0.68	1.63	2.73	3.14	3.93	5.34	5.99
	100	0.60	1.45	2.55	2.77	2.92	4.83	5.32
	130	0.62	1.59	2.68	2.85	4.20	4.99	5.45
F	50	0.51	0.96	1.39	1.90	1.49	1.42	1.41
	80	0.52	0.97	1.46	1.41	1.03	1.10	1.12
	90	0.46	0.90	1.30	1.39	1.27	1.07	1.00
	120	0.47	0.88	1.51	1.42	1.29	1.05	1.00
G	70	0.38	0.69	0.83	0.73	0.63	0.49	0.50
	90	0.31	0.49	0.78	0.52	0.41	0.21	−0.08
	100	0.15	0.22	0.54	0.22	−0.09	−0.54	−1.25
	130	0.48	0.61	0.78	0.17	−0.16	−0.61	−1.24
H	90	0.45	1.26	2.07	3.31	4.07	4.59	5.40
	150	0.38	1.07	1.71	2.47	3.28	4.43	5.14
	180	0.33	1.00	1.79	2.55	3.37	4.10	4.41
	210	0.02	1.30	2.34	2.95	3.21	3.60	3.72
I	30	0.89	1.35	..	..	..	..	..
	50	1.03	1.48	..	..	..	..	..
	60	1.15	1.65	..	..	..	..	..
	90	0.74	0.95	..	..	..	..	..

Compounds B, C, and F behaved similarly to A. In the case of D the results were erratic. Moisture was more effective in reducing oxidation in compound G than any other, and the physical results for this compound were especially good in the wet atmosphere. The large increases in weight

[8] Ind. Eng. Chem., **18**, 224 (1926).


CURVE 1
SAMPLE A-60' CURE
CURVE 2
SAMPLE A-100' CURE
CURVE 3
SAMPLE A-110' CURE
CURVE 4
SAMPLE A-130' CURE
TENSILE STRENGTH IN POUNDS PER SQUARE INCH
TENSILE STRENGTH IN KILOGRAMS PER SQUARE CENTIMETER
% ELONGATION
0
150
300
450
600
750
400
800
1200
1600
2000
2400
2800
3200
28
56
85
113
141
169
197
226
O
W


CURVE 5
SAMPLE B-50' CURE
CURVE 6
SAMPLE B-80' CURE
CURVE 7
SAMPLE B-90' CURE
CURVE 8
SAMPLE B-120' CURE
TENSILE STRENGTH IN POUNDS PER SQUARE INCH
TENSILE STRENGTH IN KILOGRAMS PER SQUARE CENTIMETER
% ELONGATION
0
150
300
450
600
750
400
800
1200
1600
2000
2400
2800
3200
28
56
85
113
141
169
197
226
O
D
I
W

of E and H in the wet atmosphere year after year were probably due to hydration of the clay and magnesia.

(7) The change in weight of the rubber slabs in the dry box proved to be a good criterion of the deterioration during aging (Curve 24 and Table V). This conclusion would be less reliable where moisture was present, because of the influence of varying amounts of hygroscopic material.

When the test slabs in the dry box have increased 1 per cent in weight calculated on the rubber in the compound, they have lost about 50 per cent of their reënforcing properties, and they continue to lose about 50 per cent for each increase of 1 per cent in weight.

Note—In Curves 1 to 24 the heavy line shows stress-strain curve before aging. *W* is stress-strain curve obtained after 4 years' storage in a moist atmosphere; *D* is stress-strain curve obtained after 4 years' storage in a dry atmosphere; *I* is stress-strain curve obtained after 4 years' storage indoors; and *O* is stress-strain curve obtained after 4 years' storage outdoors.

II—Aging of Rubber under Strain

Light has a decided deteriorating effect on rubber under strain. Even light that has passed through a window pane, which cuts out the shorter wave lengths, causes cracking.

Since this kind of aging is believed to be different from aging "on the shelf," tensile test pieces of each cure were fastened to boards under initial strains of 50 and 200 per cent elongation, and one of the sets of test pieces was placed on the roof in the sunlight and the other in the dark in a loft over the laboratory.

The test pieces that were exposed to the sun and weather showed a considerable variation in resistance to light. Compound D, which contained no pigment, failed within a few hours and the opening of the cracks could be watched. Compound C, with only zinc oxide for activation, showed slightly greater resistance to the light, and the other compounds showed a marked superiority, especially compound F which contained paraffin. The value of paraffin in this respect is well recognized by rubber technologists.

Qualitative observations with the non-pigmented compound (D) showed that the destruction was especially rapid on a hazy day—this may be attributed to humidity. It seems probable that accelerated aging tests where the rubber compounds have been exposed to light have not given sufficient attention to the moisture content of the rubber and the atmosphere. At the end of about $1^1/_2$ years all the samples except a few of F compound had broken or had assumed a set so high that the stress had become practically zero. The exact number of days for each piece to break is given in Table VI.

The samples were left in this condition for 4 years and 10 months, when the test pieces that had not failed were tested for tensile properties. The results of the tests are given in Table VII. The surface of these test pieces was checked and a chalky layer 0.01 inch (0.25 mm.) deep was

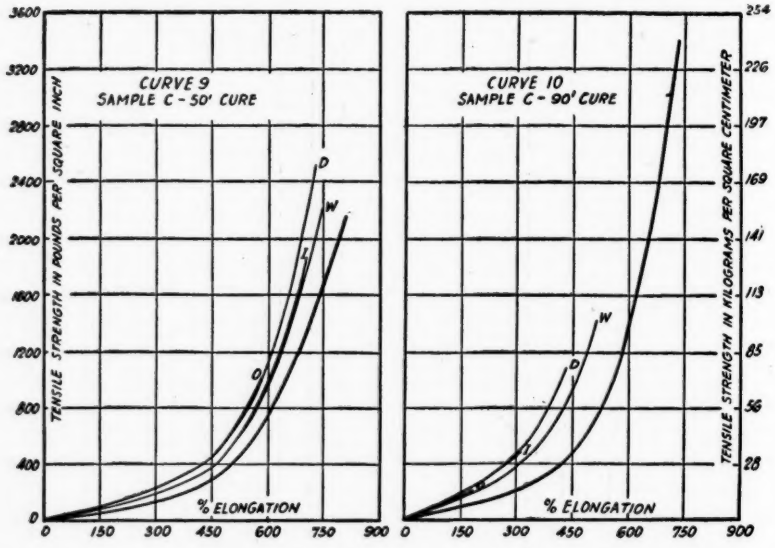
Table V—Relation of Change in Weight to Decrease in Area under Stress-Strain Curve of Test Pieces Stored in a Dry Atmosphere

Cure	After 2 Years' Aging									After 4 Years' Aging								
	A	B	C	D	E	F	G	H	I	A	B	C	D	E	F	G	H	I
	Per cent decrease in area under stress-strain curve																	
Under	8	−12	−10	9	35	−16	−10	−4	−36	7	−13	−25	46	68	−40	4	−7	−40
Intermediate	29	5	52	71	64	3	44	41	17	40	20	66	98	80	8	78	68	−3
Intermediate	43	33	72	90	70	23	69	63	10	51	47	93	99	89	32	86	71	13
Over	61	68	96	98	86	58	81	81	70	63	87	99	99	94	66	86	93	89
	Per cent increase in weight calculated on basis of 100% rubber																	
Under	0.07	−0.10	−0.10	0.14	1.40	−0.10	0.61	0.38	..	0.34	0.22	0.24	0.62	2.63	0.15	1.15	0.74	..
Intermediate	0.54	0.07	0.72	0.98	1.54	0.56	0.98	0.91	..	0.98	0.56	1.34	3.89	2.75	0.68	2.00	1.67	..
Intermediate	0.68	0.82	0.97	1.22	2.38	0.29	1.58	1.40	..	1.12	1.62	2.01	..	3.23	0.71	3.46	3.07	..
Over	1.10	2.08	1.59	2.06	2.57	0.54	2.65	3.38	2.59	2.09	3.61	3.52	3.92	3.44	1.20	4.87	5.88	..

found. The cross section of the solid center of the test piece that had been stretched to 200 per cent elongation was about 0.08 by 0.04 inch (2.03 by 1.02 mm.). A tensile force of $2^2/_3$ pounds (1.2 kg.) was required to break it, which calculates to 835 pounds per square inch (59 kg. per sq. cm.). This is a remarkable figure considering the aging exposure and speaks well for the protection afforded by the white pigment and the paraffin.

Tener, Smith, and Holt[9] have stated that dark-colored compounds are more resistant to sunlight than light-colored compounds. However, they used whiting in their work, whereas the writers used zinc oxide.

Stutz[10] has shown that there is a considerable difference in the opacity of these pigments to the short wave lengths of light, zinc oxide being entirely opaque at the shorter wave lengths whereas whiting is quite transparent. He has also



shown that zinc oxide protects a paint film against chalking while pigments that are transparent at the shorter wave lengths fail to protect.

The protection given to rubber by zinc oxide is the same as that given to a paint vehicle. The color of the rubber compound in itself is of secondary importance in resistance to sunlight. The important factor is the opacity of the pigment to the particular wave lengths of light that are injurious.

Jecusco[11] has made a good start along this line in studying the deterioration of rubber caused by light through investigating the aging effect of different wave lengths.

[9] *Bur. Standards, Tech. Paper* **342**.
[10] *J. Franklin Inst.*, **200**, 87 (1925).
[11] IND. ENG. CHEM., **18**, 420 (1926).

This kind of deterioration has been a much more important problem to the paint chemist than to the rubber chemist, as the paint chemist is largely interested in surfaces. He has done a great deal of work on accelerated tests and we can profit by studying some of his methods.[12]

Only a few test pieces which were exposed in the dark were broken after $3^1/_2$ years. Those that did break were the ones that had been given an initial strain of 200 per cent elongation.

Table VI—Days Required for Failure of a Test Piece Exposed to Weather under Strain

Comp.	50% Elongation				200% Elongation			
A	*60*[a]	*100*	*110*	*130*	*60*	*100*	*110*	*130*
	265	308	288	255	260	219	216	219
	274	344	294	304	265	222	211	224
	353	275	285	264	255	221	211	224
B	*50*	*80*	*90*	*120*	*50*	*80*	*90*	*120*
	285	275	304	241	236	224	225	217
	353	501	281	304	239	217	227	212
	366	285	305	229	243	231	219	214
C	*50*	*90*	*100*	*120*	*50*	*90*	*100*	*120*
	...	...	...	299	213	80(?)	65(?)	73(?)
	...	...	...	...	209	37	41	67
	...	...	...	245	229	4	4	1
D	*180*	*240*	*270*	*330*	*180*	*240*	*270*	*330*
	...	...	...	...	221	31	37	1
	...	...	...	...	221	265	2	1
	...	...	602	635	265	1	1	1
E	*60*	*90*	*100*	*130*	*60*	*90*	*100*	*130*
	...	658	391	635	230	210	211	351
	740	...	...	314	338	215	198	...
	...	...	635	...	224	229	212	203
F	*50*	*80*	*90*	*120*	*50*	*80*	*90*	*120*
	...	...	...	...	...	...	602	217
	...	...	...	...	...	366	358	211
	...	...	...	...	...	635	602	212
G	*70*	*90*	*100*	*130*	*70*	*90*	*100*	*130*
	233	635	286	258	222	208	208	206
	305	339	635	262	224	209	209	200
	314	635	305	286	210	209	207	205
H	*90*	*150*	*180*	*210*	*90*	*150*	*180*	*210*
	740	...	789	...	224	184	198	49
	...	...	...	...	246	198	67	43
	...	602	...	...	238	200	200	31
I	*30*	*50*	*60*	*90*	*30*	*50*	*60*	*90*
	501	662	539	323	239	227	214	198
	635	662	635	391	232	231	205	200
	635	501	635	398	538	228	209	200

[a] Numbers in italics refer to minutes' cure at 40 pounds.

Whereas in sunlight overcures checked more rapidly than undercures, in the dark the reverse was the case. This was only a surface effect, however, and after $3^1/_2$ years of strain the undercures generally tested stronger than the overcures.

The distance between the marks on the tensile-strength test pieces, which were originally 3.81 cm. (1.5 inches) and 7.62 cm. (3 inches) in the stressed position, increased as time went on. Owing to the greater strain in the thin section of the test piece, this part weakened more than the thicker ends and in turn stretched further. The set on release was accordingly in many cases greater than the original amount of elongation.

[12] Nelson and Schmutz, Ind. Eng. Chem., **18**, 1222 (1926).

III—Comparative Aging of Cured and Uncured Rubber

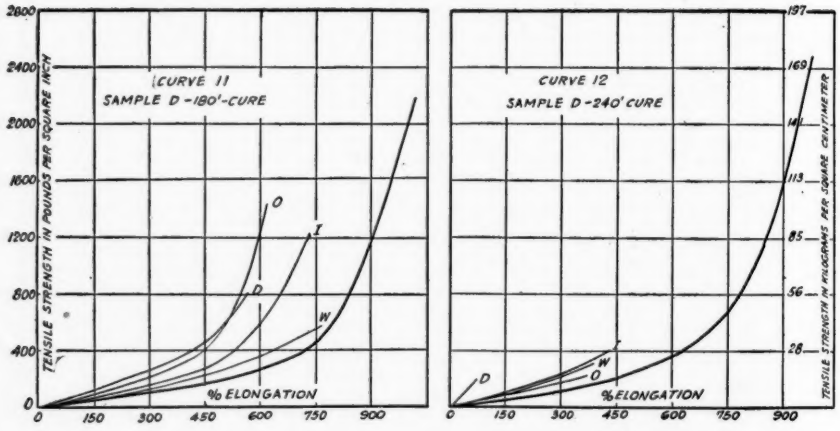
The uncured stock left after making the slabs required in the preceding part of this work was wrapped in holland cloth and stored in a dark room in the laboratory for 18 and 36 months before curing.

The results of this storage are given in Table VIII. On comparing tests made on slabs cured up at the time of milling with similar stocks stored in the uncured state for 18 and 36 months and then cured, the following facts are noted:

(1) The optimum for the samples cured and tested 24 and 48 hours after milling was generally one of the two intermediate cures.

(2) After aging in the cured state the optimum came at the shortest cure, which is in line with the statement of Geer and Evans[3] that overcuring is a major factor in aging.

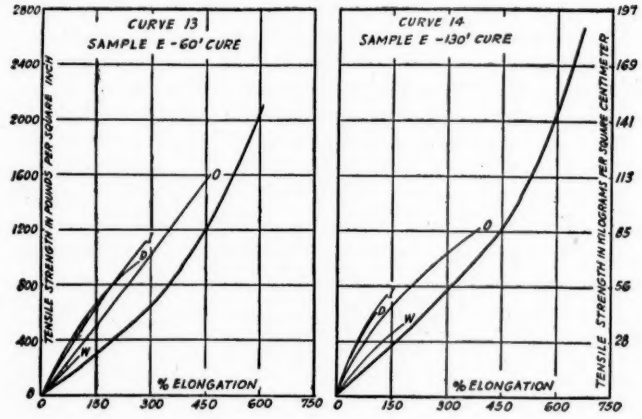
(3) The optimum in the case of the stock stored uncured occurred at the longest cure; the very reverse to the situation for storage in the cured state. Storage has retarded the cure.

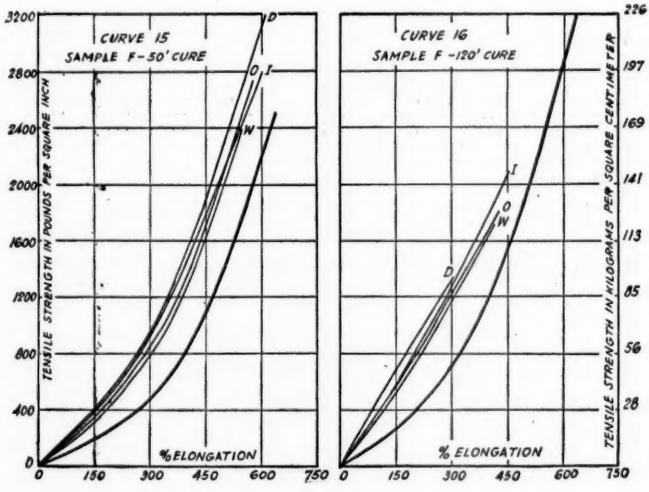


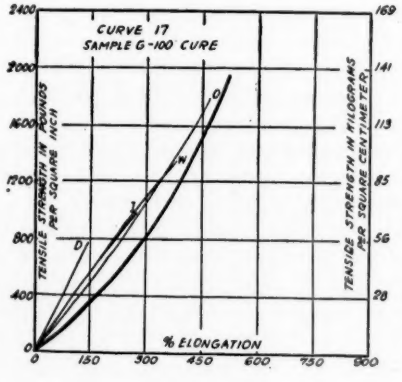
One of the stocks (G) deteriorated very appreciably in the uncured state. The reason for this peculiar behavior is an open question, but it has been generally observed that master batches of crude rubber with certain accelerators become very soft and sticky in a short time.

The most probable cause for the retardation in cure is the formation of sulfurous and sulfuric acid due to the oxidation of some of the sulfur in the compound. A second possibility is that the organic accelerator decomposes during storage. The fact that this retardation occurred in the case of compounds D and H, which contain no added organic accelerator, is partial negative evidence in favor of the first explanation.

Some clay and carbon black stocks show a rapid retardation that has been attributed to adsorption of the accelerator by the pigment. Since the retardation is pronounced in the


CURVE 13
SAMPLE E - 60' CURE
TENSILE STRENGTH IN POUNDS PER SQUARE INCH
% ELONGATION
CURVE 14
SAMPLE E - 130' CURE
TENSILE STRENGTH IN KILOGRAMS PER SQUARE CENTIMETER
% ELONGATION


CURVE 15
SAMPLE F - 50' CURE
TENSILE STRENGTH IN POUNDS PER SQUARE INCH
% ELONGATION
CURVE 16
SAMPLE F - 120' CURE
TENSILE STRENGTH IN KILOGRAMS PER SQUARE CENTIMETER
% ELONGATION


CURVE 17
SAMPLE G - 100 CURE
TENSILE STRENGTH IN POUNDS PER SQUARE INCH
TENSILE STRENGTH IN KILOGRAMS PER SQUARE CENTIMETER
% ELONGATION

case of C, which contains practically no pigment, the adsorption explanation does not apply in this case.

The extent of the retardation during the first 18 months is much greater than during the second 18 months.

The retardation of cure on storage of the uncured stock makes the practice of aging stocks for two or more weeks between milling and processing rather questionable. Certainly, if this is done it will be quite advantageous to keep this period constant.

Table VII—Physical Properties after Straining Test Pieces in Light for 4 Years and 10 Months

Sample	Time of Cure at 141.5° C.	Set	Thickness after Release of Tension		Load at Break	Tensile Strength[a]		Elongation at Break[b]
			Shoulder of tensile	Middle of tensile				
	Min.	%	*Cm.*	*Cm.*	*Kg.*	*Kg./sq. cm.*	*Lbs./sq. in.*	%
			STRETCHED 50 PER CENT					
F	50	85	0.384	0.312	4.4	18	255	460
	80	87	0.368	0.277	3.5	15	210	345
	90	87	0.351	0.251	3.0	13	190	280
	120	85	0.353	0.269	3.5	15	220	185
			STRETCHED 200 PER CENT					
F	50	235	0.366	0.183	1.2	5	70	400
	80	...	...	...	...	..	...	...
	90	...	...	...	...	..	...	...
	120	...	...	...	...	..	...	...

[a] Based on initial width and thickness.
[b] Based on marks originally 2.54 cm. apart.

It is also important to know whether the reënforcing properties have been affected by storage of the uncured stock. If not, it should be possible to bring the uncured stock back to practically its initial condition by adding organic accelerator.

The data in Table IX show that, although the initial properties can be nearly restored by this method, the stiffness of the stock especially at the higher cures, is greater, and the percentage elongation at break is less. It was also noted that the aged compound was sticky, and the added accelerator had to be milled in at low temperatures to prevent the stock from sticking to the back roll of the mill.

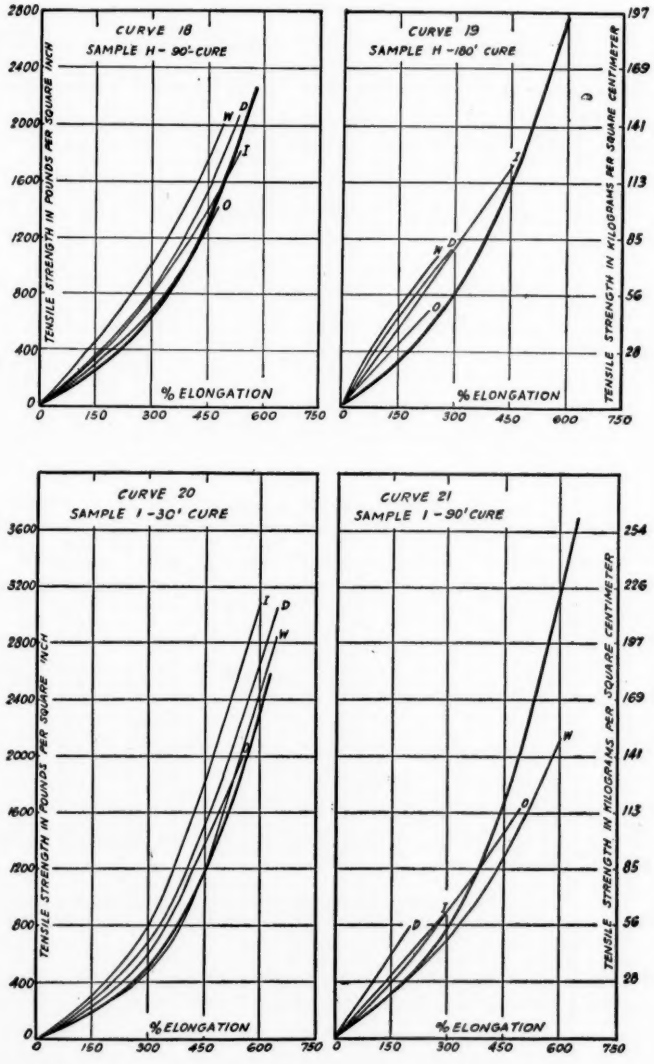
In the writers' opinion the deterioration in physical properties, though important, is secondary to the retardation of cure.

Conclusions

Part I—Compounded cured rubber stored in a wet box has a softer stress-strain curve than when stored in a dry box. If dried after a long exposure to a moist atmosphere the tensile strengths increase by 21 to 28 kg. per sq. cm. (300 to 400 pounds per square inch).

On a basis of tensile tests, overcured rubber deteriorates faster in a dry atmosphere than in a wet atmosphere and the reverse is the case for undercures. An undercure will oxidize at about the same rate in a wet as in a dry atmosphere, but an overcure will oxidize more rapidly in the dry atmosphere as shown by changes in weight.

The change in weight of samples stored in a dry box, which excludes moisture changes, proved a good criterion of their deterioration. Each increase of 1 per cent in weight calculated on the rubber content showed a corresponding decrease in reënforcing properties of 50 per cent.



PART II—The ability of zinc oxide and paraffin to protect rubber under strain against sunlight was shown and it was suggested that humidity was a factor. The protection that pigments offer against sun-cracking is the same in both paint

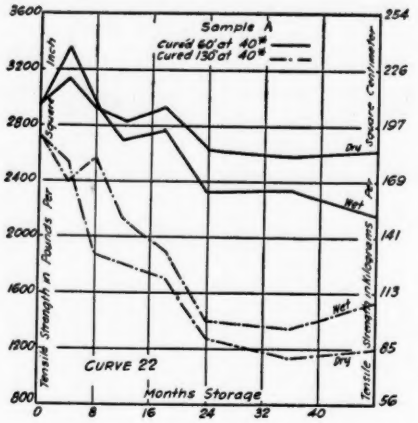
Table VIII—Relative Aging of Cured and Uncured Compounds

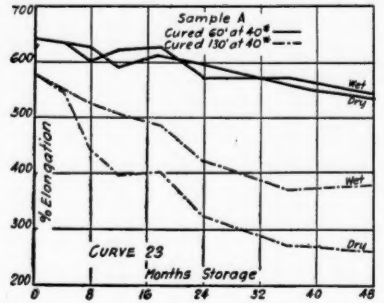
Comp.	Time Cure at 40 Lbs.	Original			After 18 Months' Aging Indoors						After 36 Months' Aging					
					Cured			Uncured			Cured			Uncured		
		Tensile strength	Elong.	Load at 300% elong.	Tensile strength	Elong.	Load at 300% elong.	Tensile strength	Elong.	Load at 300% elong.	Tensile strength	Elong.	Load at 300% elong.	Tensile strength	Elong.	Load at 300% elong.
	Min.	*Lbs./sq. in.*	*%*	*Lbs./sq. in.*	*Lbs./sq. in.*	*%*	*Lbs./sq. in.*	*Lbs./sq. in.*	*%*	*Lbs./sq. in.*	*Lbs./sq. in.*	*%*	*Lbs./sq. in.*	*Lbs./sq. in.*	*%*	*Lbs./sq. in.*
A	60	2940	640	615	3100	640	595	2165	590	505	2655	565	775	2150	595	610
	100	3020	630	730	2485	575	960	2910	620	685	1905	455	1090	2435	585	785
	110	2715	585	815	2370	530	1000	2945	610	720	1920	475	1050	2415	565	760
	130	2725	575	865	1915	475	1050	3125	610	785	1460	355	1215	2530	590	825
B	50	2830	650	495	3090	620	760	1770	570	470	2675	580	815	1505	560	495
	80	3040	610	705	2490	530	1000	2845	630	600	2285	485	1140	2215	575	760
	90	3095	620	675	2370	525	1045	2845	605	710	1910	430	1130	2135	570	705
	120	3050	590	800	1375	350	1195	3085	605	765	855	215	..	2295	590	655
C	50	2155	805	140	2185	780	155	1330	830	90	1450	690	135	1000	840	75
	90	3400	730	220	2050	600	300	1535	710	145	610	415	345	2110	775	185
	100	3165	735	260	1865	555	365	2325	735	190	435	370	290	1850	735	180
	120	3135	685	305	265	195	..	2280	735	135	335	260	..	2765	740	230
D	180	2165	1020	100	2020	1000	100	1750	990	...	1840	855	160	Stock lost		
	240	2470	980	120	1590	760	100	2025	985	35	1470	760	180			
	270	2800	945	130	1785	835	90	540	890	85	190	410	220			
	330	2425	890	150	275	490	125	1155	880	95	245	120	..			
E	60	2115	610	660	2175	590	840	1705	575	540	1610	435	1170	1670	480	810
	90	2210	635	680	1865	540	990	2145	635	710	1000	245	..	2105	535	980
	100	2175	650	715	1670	510	935	2325	685	700	890	195	..	2230	560	985
	130	2650	670	795	1290	370	1095	2535	670	815	710	160	..	2460	595	1000
F	50	2500	635	455	2615	605	655	900	485	310	2765	580	825	1595	600	300
	80	2880	630	645	3005	610	820	2040	580	505	2645	560	770	1975	580	570
	90	3180	635	675	3135	615	930	2250	595	470	2430	550	1020	2130	585	680
	120	3190	635	700	2835	595	745	2595	620	655	2035	480	1075	2150	565	615
G	70	1645	530	640	1520	535	645	[a]			1160	435	830	[a]		
	90	2075	560	720	1395	440	865				1150	345	1030			
	100	1955	520	810	1630	460	980				1040	295	..			
	130	1475	420	1085	900	250	..				765	170	..			
H	90	2260	580	625	2435	635	580	1735	535	605	1700	510	660	1355	525	470
	150	2690	640	655	2665	595	825	2130	560	730	1745	475	895	1710	525	680
	180	2765	600	820	2335	570	925	2270	550	820	1875	460	980	1935	525	775
	210	2380	600	795	1375	435	980	2335	580	840	700	170	..	2085	560	750
I	30	2580	625	470	3200	590	700	1370	515	345	2985	605	715	1510	595	185
	50	3440	645	625	3050	595	730	1960	555	500	3060	605	730	2305	630	300
	60	3495	630	740	2780	545	960	2265	540	695	2405	505	1000	2465	610	490
	90	3690	645	770	2090	475	990	2565	600	680	1615	460	1030	2900	650	540

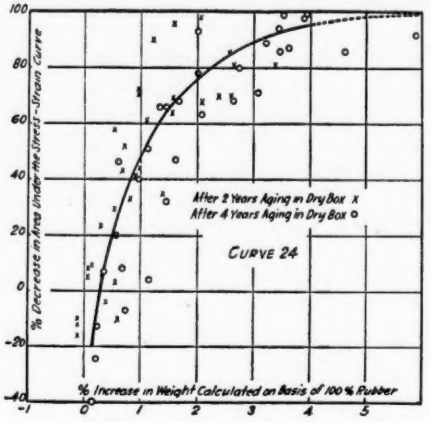
[a] The aged uncured stock was very tacky, stuck to cloth, and cured porous.

Table IX—Effect of Adding Accelerator to Aged Uncured Rubber

When Cured	Compound A				Compound C			
	Time of cure at 40 lbs.	Tensile strength	Elong.	Load at 300% elong.	Time of cure at 40 lbs.	Tensile strength	Elong.	Load at 300% elong.
	Min.	*Lbs./sq. in.*	*%*	*Lbs./sq. in.*	*Min.*	*Lbs./sq. in.*	*%*	*Lbs./sq. in.*
Directly after mixing	60	2940	640	615	50	2155	805	140
	100	3020	630	730	90	3400	730	220
	110	2715	585	815	100	3165	735	260
	130	2725	575	865	120	3135	685	305
After 67 months' storage uncured	60	2130	560	655	50	1440	885	115
	100	2300	530	890	90	2440	775	150
	110	2520	550	910	100	2500	745	160
	130	2385	535	930	120	2620	715	230
After 67 months' storage uncured with the addition of 0.16% hexa calculated on rubber (1/4 original amount added)	60	2020	555	660	50	1820	890	80
	100	2520	545	970	90	2680	760	195
	110	2495	535	1000	100	2890	735	240
	130	2350	515	1100	120	3140	730	245
After 67 months' storage uncured with the addition of 0.32% hexa calculated on rubber	60	2460	600	660	50	2100	815	115
	100	2620	560	945	90	2700	655	275
	110	2610	555	970	100	3160	680	310
	130	2500	525	1085	120	2560	620	370
After 67 months' storage uncured with the addition of 0.65% hexa calculated on rubber	60	2545	585	755	50	2230	805	155
	100	2880	550	1045	90	2640	655	280
	110	2880	535	1140	100	3240	665	340
	130	2710	515	1230	120	2320	595	420


Sample A
Cured 60' at 40#
Cured 130' at 40#
Tensile Strength in Pounds Per Square Inch
Tensile Strength in Kilograms Per Square Centimeter
Dry
Wet
Wet
Dry
CURVE 22
Months Storage
3600
3200
2800
2400
2000
1600
1200
800
254
226
197
169
141
113
85
56
0
8
16
24
32
40


Sample A
Cured 60' at 40#
Cured 130' at 40#
% Elongation
Wet
Dry
Wet
Dry
CURVE 23
Months Storage
700
600
500
400
300
200
0
8
16
24
32
40
48


% Decrease in Area Under the Stress - Strain Curve
After 2 Years Aging in Dry Box X
After 4 Years Aging in Dry Box O
CURVE 24
% Increase in Weight Calculated on Basis of 100 % Rubber
100
80
60
40
20
0
-20
-40
-1
0
1
2
3
4
5

and rubber, and the large amount of work done by the paint chemist should be studied by the rubber technologist.

PART III—The effect of aging unvulcanized compounded rubber is to retard the cure greatly and to lower the reënforcing properties slightly. Unvulcanized compounded rubber that has lain around in holland cloth for several years is sticky and has to be milled on cold rolls, but after adding accelerator and vulcanizing a good product is obtained. The retardation, in this program, is not due to adsorption of accelerator by the pigment since some of these stocks are practically "pure gum" stocks.

If this program on "normal aging" were being started today, all of these nine compounds would not have been chosen; other formulas would have been used containing antioxidants that were unknown six years ago; certain new accelerators would have been used; and hygroscopic[6] reclaim stocks would have been added.

Acknowledgment

The writers wish to acknowledge the assistance of Howard Hock, who drew the curves shown in this article and helped in making the tests.

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Carbon Blacks and Their Use in Rubber[1]

I—Comparative Properties of Blacks and Tests in Uncured Rubber

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The physical and chemical characteristics of several carbon blacks and of rubber stocks containing them have been investigated in order to determine their suitability as pigments in tire-tread stocks. Five blacks have been studied—Charlton lampblack, Micronex, Super Spectra, Thermatomic, and Goodwin. Part I represents a study of the properties of the blacks themselves and their use in raw rubber. Part II, to be published in a subsequent issue, will describe tests on various cured rubber stocks containing the same blacks.

OUR knowledge regarding the physical and chemical characteristics of pigments which make them more or less suitable as reënforcing agents in cured rubber goods is very incomplete. In spite of several brilliant contributions in the field, we are still far from a satisfactory understanding of the principles involved in the preparation of compounds. Lack of systematically arranged information is perhaps partly responsible for this state of affairs. The object of this paper was to assemble more detailed and well-organized information in a small field. It is believed that a sufficient number of systematic efforts will place us in a position to understand more completely the colloidal behavior of pigments in rubber and perhaps in other media.

[1] Received January 30, 1928.

This study has been confined to the pigments most commonly used in tire treads—namely, carbon blacks—although in rare cases other pigments have been introduced to illustrate some particular point. It is hoped that a few attempts to explain experimental results where the information is not complete will be excused in consideration of the chief aim of the work, which is only to point out the facts, for the authors realize that certain conclusions may have to be qualified as new information becomes available.

Five blacks having as widely different characteristics as possible have been chosen for study:

(1) Charlton lampblack—An oil black.
(2) Micronex—A channel-process gas black, made for and widely used by the rubber trade.
(3) Super Spectra—A channel-process gas black made for use in varnishes and enamels.
(4) Thermatomic—A gas black made by thermal decomposition of natural gas.
(5) Goodwin—A gas black made by incomplete combustion of natural gas at high temperature.

It was hoped that, by comparing a large number of the various physical and chemical properties of the blacks with the physical properties of vulcanizates prepared from them, some relationships between the two sets of properties might become apparent.

Characteristics of Blacks

TRUE SPECIFIC GRAVITY—The determination of specific gravity was carried out at 15° C. in a pycnometer bottle upon a sample dried at 105° C. Xylene was used as the liquid displaced. The ease of wetting and the higher temperature made available through the use of this liquid facilitated the expulsion of entrained or absorbed gases. The blacks were always heated in contact with xylene, allowed to stand overnight, and heated again before the measurements were made. The values thus determined are given in Table I. It appears from the work of Lowry[2] that values obtained by this method are satisfactory, and they are therefore used throughout all subsequent calculations.

Table I—Specific Gravities of Blacks

BLACK	SAMPLE A	SAMPLE B	AVERAGE
Charlton	1.65	1.67	1.66
Charlton extracted with acetone	1.72	1.70	1.71
Micronex	1.78	1.80	1.79
Super Spectra	1.87	1.90	1.89
Thermatomic	1.84	1.84	1.84
Goodwin	1.83	1.80	1.82

The difference in gravity among the various samples is not a new observation,[3] nevertheless it is a rather curious result. It may be due to a variety of causes, such as incomplete wetting by the displaced liquid; inhomogeneity of the individual carbon particle, which is said to contain an appre-

[2] *J. Am. Chem. Soc.*, **46**, 824 (1924).
[3] Neal and Perrott, *Bur. Mines, Bull.* **192** (1922).

ciable amount of hydrocarbons either as admixed or adsorbed material; or to pore size within the individual particle. These problems have been discussed at some length by Lowry[2] and others. The temperature of formation of the blacks does not in this case seem to be connected with their densities, as would be expected from the work of Roth, Naeser, and Döpke.[4]

APPARENT SPECIFIC GRAVITY—This quantity was obtained by tapping the black down in a 400-cc. Erlenmeyer flask and adding to keep to the mark until 10 minutes additional tapping produced no further settling. The results as given in Table II represent the condition of the black as delivered and might be considerably altered by compression. The relative bulk volume settled from a liquid should give the relation more satisfactorily than the apparent density in air. Samples which were well dispersed in mineral oil and allowed to settle for about 3 months gave the approximate relative densities shown in Table III.

Table II—Apparent Density of Blacks

BLACK	*Gram per cc.*
Charlton	0.15
Micronex	0.26
Super Spectra	0.11
Thermatomic	0.65
Goodwin	0.12

Table III—Relative Densities as Settled in Liquid

	Gram per cc.
Charlton	0.35
Micronex	0.40
Super Spectra	0.30
Thermatomic	1.00
Goodwin	0.45

ASH—The ash was determined by igniting 2 to 10 grams of material to constant weight in a porcelain crucible over a Fisher burner. All values are on a moisture-free basis.

Table IV—Ash

BLACK	ASH	REMARKS
	Per cent	
Charlton	0.08	Reddish, quite gritty
Micronex	0.01	Reddish, trace of grit
Super Spectra	0.08	Reddish, free from grit
Thermatomic	0.04	Gray, small pellets fused to crucible
Goodwin	0.04	Reddish brown, slight grit

FINENESS OF DIVISION—Figure 1 shows photographs of the blacks made with dark field illumination. The method of preparation and mounting was as follows: Two grams of black were milled into 100 grams of clean pale crepe. Two grams of this batch were added to 25 cc. of xylene in a sample bottle and allowed to stand with occasional shaking until dispersion was complete. A small drop was then placed upon a slide, covered, and pressed under a 500-gram weight for 3 hours, by which time flow had ceased. The available equipment prevented any more accurate method, but without doubt the fields represented in the figure contain approximately equal weights of black. The method therefore gives, if not the actual particle size, at least the order in which the blacks fall. The order of increasing particle size is Super Spectra, Micronex, Goodwin and Charlton about equal, Thermatomic. The particles of Super Spectra are so fine that they were photographed with difficulty

[4] *Ber.*, **59**, 1379 (1926).

and the foggy results here shown is the best of several attempts.

DISPERSION—These photographs do not represent the dispersion of the black in the original rubber black mix. In the xylene solution the blacks all slowly flocculate and must be agitated before the mounts are made. The Thermatomic sample shows a small floccule. This could easily be broken by agitation. It is hoped that a careful study of this flocculating tendency may give some interesting information. In spite of excellent work by Green,[5] Spear,[6] and others, no entirely satisfactory method has been developed for studying the dispersion of black in cured stocks. All methods proposed make use of swelling or some mechanical distortion and seem open to question on this account.

PARTICLE SIZE FROM STRESS-STRAIN CURVE—The method of determining particle size or surface developed by a study of the stress-strain curve[7] does not give satisfactory results in the case of these blacks. It will become evident from the resilient energy data to be presented that the order of particle size would depend to a large extent upon the standard mixing which was chosen.

X-RAY EXAMINATION—W. G. Wykoff, formerly of the Geophysical Laboratory, kindly made a preliminary x-ray examination of the five samples. He notes that all samples give the same type of pattern with a breadth of line which follows the estimated order of particle size given above. Thermatomic is very much sharper than any of the others and shows several additional lines, which may not be new ones but brought out by the sharpening of the diffraction pattern. The information here outlined seems to be in essential agreement with the results obtained at the Woolwich Arsenal.[8]

It seems to be essential to further progress that we have more definite information as to the structure of the carbon-black particle. Is carbon black essentially graphitic with an admixture of hydrocarbon and gases within the particle structure, or does it consist largely of material of a nature essentially different from the known varieties of crystalline carbon? Whether x-ray diffraction patterns will give us this information depends upon the capacity of the method to distinguish between truly amorphous material (unordered atomic arrangement in the particle) and crystalline material in an exceedingly fine state of division. While the preponderance of opinion is that both carbon black and charcoal are largely graphite, the evidence at hand is not altogether convincing and authorities are not in complete agreement.[9]

[5] J. IND. ENG. CHEM., **13**, 1130 (1921).

[6] *Ibid.*, **17**, 926 (1925).

[7] Weigand, *Can. Chem. J.*, **4**, 160 (1920).

[8] Pickles, *Trans. Inst. Rubber Ind.*, **2**, 85 (1926).

[9] Debye and Scherrer, *Physik. Z.*, **18**, 291 (1917); Asahara, *Japan. J. Chem.*, **1**, 35 (1922); Howard and Hulett, *J. Phys. Chem.*, **28**, 1082 (1924); Ruff, Schmidt, and Olbrich, *Z. anorg. allgem. Chem.*, **148**, 313 (1925); Clark, IND. ENG. CHEM., **18**, 1131 (1926).

Charlton Micronex Super Spectra Thermatomic Goodwin

Figure 1—Photographs of Blacks at 860 ×

TINTING STRENGTH—To determine tinting strength 0.50 gram of carbon black was mixed with zinc oxide in boiled linseed oil until a standard color intensity was reached. Micronex with 2 grams of zinc oxide was used as the standard. The accuracy of the method is impaired by the difference in tone of the various blacks, but unquestionably puts them in the proper order. The results are given in Table V.

Table V—Tinting Strength

BLACK	OIL USED	ZINC OXIDE	RELATIVE TINTING STRENGTH
	Drops	*Grams*	
Charlton	60	1.275	0.63
Micronex	60	2.000	1.00
Super Spectra	60	1.778	0.88
Thermatomic	20	0.263	0.13
Goodwin	40	0.996	0.50

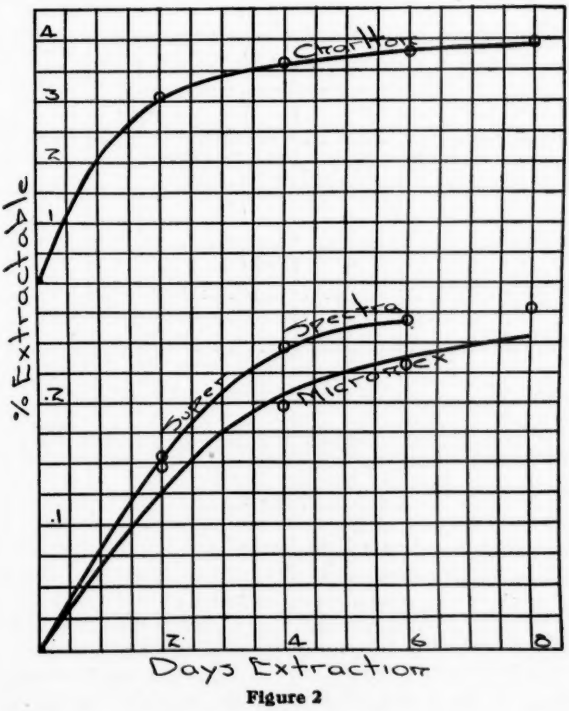

Figure 2

This is probably an indication of particle size except for the case of Super Spectra, where the black may be so finely divided as to have passed the optimum obscuring power.

LIGHT SCATTERING AND ABSORPTION—It is possible to detect the undertone of the blacks in various ways. When the black is being milled into rubber in a small quantity, a small sheet of rubber stretched out to very thin section gives it nicely. Another good method is to observe by transmitted light the color of a very dilute solution of a rubber-black mix-

ture in benzene. Tap-outs were made with the black in boiled linseed oil and also with 1 part of black to 100 parts of zinc oxide in linseed oil. All methods agree in distinguishing a reddish or yellowish brown undertone for Super Spectra and a brown for Micronex. Goodwin and Charlton are close together, with more of a blue tinge, and Thermatomic is definitely blue.

PARTICLE SHAPE—It seems highly probable that all samples are in some degree crystalline. Whether, as noted before, the particles are all crystalline and of very fine particle size,[10] or whether they contain a mixture of crystalline and amorphous carbon containing enclosed hydrocarbon is an open question. When the particles are in sluggish, Brownian motion, they give rise to a twinkling effect, which might be interpreted as due to their turning end over end with a

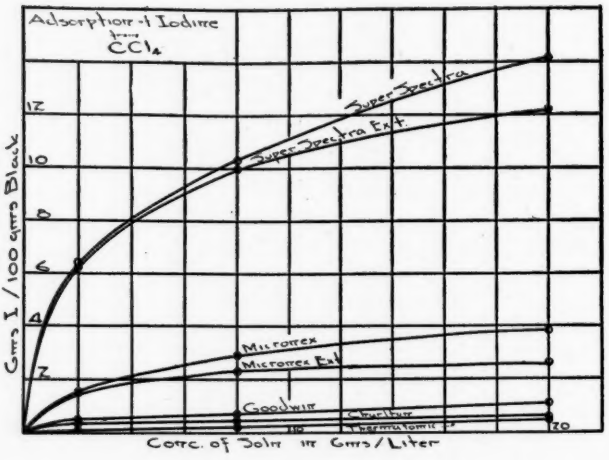

Figure 3

consequent variation in light intensity. The difference in the position of the stress-strain curve of rubber samples cut with and across the calendar grain indicates anisotropy, although the effect is much less strong than in clay or even in zinc oxide samples, in which rod-shaped particles predominate.[11]

EXTRACTABLE MATTER—The determination of acetone extract is much more difficult than seems to be generally appreciated. The usual method is outlined by Neal and Perrott.[3] The present writers' experience with acetone extraction is very interesting in the light of this method.

During some of their work it was desirable to have samples of extracted Charlton black. A small sample of perhaps 50 grams was placed in a Soxhlet apparatus and given what was considered an exhaustive extraction of about 6 or 7 days.

[10] Finely divided graphite with a relatively high adsorptive capacity has been described by Lowry and Morgan, *J. Phys. Chem.*, **29**, 1105 (1925).

[11] Vogt and Evans, IND. ENG. CHEM., **15**, 1015 (1923).

After several months this sample was again used for another purpose from that originally designed, and it was found that color was extracted from the black by the medium in which it was used. Part of the sample was further extracted for 10 to 12 days. The extract was deeply colored and at the end of this time a fresh flask and a fresh supply of acetone were tried. Several days more of extraction gave a very decided color to this batch of acetone. When a portion of this extract-containing acetone was added to some of the original sample with only the initial 6 or 7 days' extraction, the color was partially removed from the solution.

Qualitative experiments were made upon the extraction of the blacks with xylene. After continuous extraction for 30 days the solvent was replaced with fresh solvent. At the end of 10 days' further extraction a rich color was produced in the extraction flask in each case. The order of color depth was the same as the order determined by overnight extraction with acetone in the usual quantitative way.

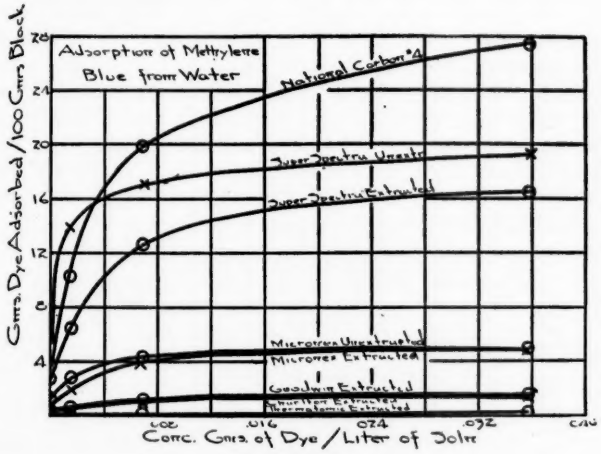

Figure 4

Another experiment was carried out to follow the rate of acetone extraction quantitatively. A 1- to 2-gram sample was placed in a double-thickness Whatman extraction thimble which was folded in and wired at the top to prevent escape of the blacks. The thimbles were then placed in an Underwriter's apparatus and extracted. Tared flasks were run for 2 days each and weighed until four flasks had been used and the total time of extraction had been 8 days. Check samples were run in all cases and the average results of two runs are plotted in Figure 2.

It is obvious from this figure that extractions of less than several days do not approach the true value and that check results may be difficult to obtain owing to varying rates of extraction under different heating conditions. It has been

suggested by the work of Firth and Watson[12] that the phenomenon of continued color extraction may be due to the catalytic effect of the carbon black in breaking down the extraction medium with the production of colored bodies. The breakdown of carbon tetrachloride when used for extraction is apparent. In view of the nature of the extracting media (acetone and xylene) and the asymptotic character of the curves of Figure 2, the phenomenon is believed to be one of extraction rather than catalytic activity. The fact mentioned above, that extracted material is re-adsorbed when placed in contact with the original sample, is further evidence that the extraction process involves an adsorption equilibrium and that the length of time necessary for extraction is due to the tenacity with which the carbon-black surface retains absorbed material.

Another difficulty which becomes serious, especially with certain blacks, during long extraction periods is the tendency of the carbon to go through the filter paper. This may be overcome by the addition of several grams of diatomaceous earth that has been exhaustively extracted. The method now in use in this laboratory is as follows: One to two grams of air-dried black are placed with 3 or 4 grams of diatomaceous earth in a double-thickness Whatman thimble, folded down and wired shut. The thimble is placed in an Underwriter's apparatus and extracted continuously for 5 days. The extract in the flask is then dried overnight at 56° C. and weighed.

The extract of the five blacks, so determined, is given in Table VI.

Table VI—Extract of Blacks

Black	Extract
	Per cent
Charlton	3.70[a]
Micronex	0.23
Super Spectra	0.27
Thermatomic	1.64
Goodwin	1.44

[a] These figures are the average of several determinations.

In the writers' opinion the amount of extractable matter stands in no relation to the quality of black. The determination of total extractable matter is practically impossible. The determination of material extracted during a given period is open to objection because the rate of extraction differs according to a number of variable conditions and checks are almost impossible to obtain. Therefore, little importance is attached to this test.

During the course of tests reported in Table VI the decrease in weight of the thimbles containing the black was also recorded, it was noticed that this decrease never equaled the gain in weight of the flasks and in some cases, notably that of Super Spectra, the extracted sample weighed more than it did previous to extraction. Water extraction generally brought this weight down below the original. These in-

[12] *J. Phys. Chem.*, **29**, 987 (1925).

creases were attributed to the retention of acetone by the blacks.

This activity of the blacks is further demonstrated by the absorption of light gasoline. Wetting of Micronex caused a 2.5 per cent increase after drying at 105° C. A sample of Super Spectra wet with light gasoline and dried at 105° C. showed an increase in weight of 8 per cent. The samples, 4 grams total, were removed to distillation flasks and distilled with glycerol up to 400° C. A distillate of approximately 0.5 cc. of yellow gasoline was obtained. This is in fair agreement with the amount calculated from the increase in weight of carbon, 0.3 gram.

ADSORPTIVE CAPACITY—The adsorptive capacity of black is an important factor in its use in rubber. The writers' studies of adsorption are not yet complete, but such data

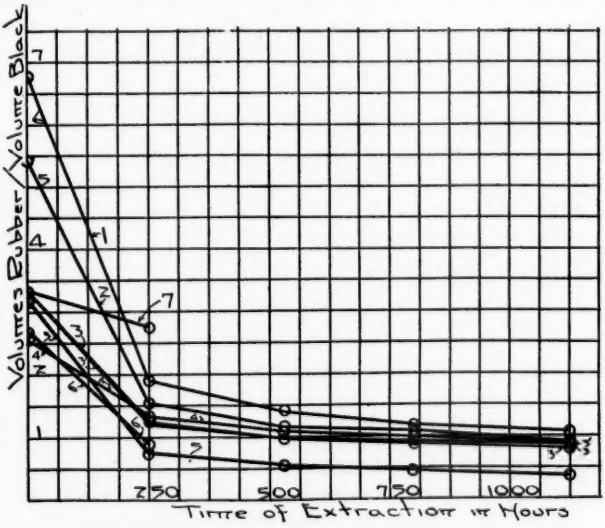

Figure 5

as have been obtained will be presented. The method was as follows: 1 gram of black was added to a bottle containing 90 cc. of the liquid medium. Some of the samples settled very slowly and 4 grams of diatomaceous earth were added to each bottle. The method of comparison was similar

Note—The difference in the behavior of diatomaceous earth in water and carbon tetrachloride is very interesting. In water true sedimentation takes place but in carbon tetrachloride floccules are formed and a sharp boundary appears between the settling material and the very clear supernatant liquid. The floccules of diatomaceous earth enclose and carry the black out of carbon tetrachloride suspension rapidly and completely. In all cases correction is made for the comparatively small adsorptive capacity of the precipitant.

to that outlined by Spear and Moore[13]—i. e., the adsorption was measured in equilibrium with a solution of known

[13] IND. ENG. CHEM., **18**, 418 (1926).

concentration. The concentrated colored solution was titrated into the bottle containing the black until the color of the supernatant liquid at equilibrium matched a standard. The titration at each equilibrium point extended for 3 days. From the total amount of material added and the concentration of the solution the amount adsorbed was calculated. Imperfect wetting of the surface of one or another of the blacks would apparently give an erroneous result for that black. Two colored materials, iodine and methylene blue, were used in two media, carbon tetrachloride and water, in order to minimize this source of error. One of the difficulties in the way of measurement of the raw blacks was the extractable matter. When working in carbon tetrachloride the extract was deeper in color than the iodine, making measurement impossible. When working in water certain of the blacks could not be wet, presumably because of the extractable material. All samples were therefore acetone-extracted continuously for not less than 3 days and, where the extract was high, for as long as 8 days.

Figure 3 shows the data for adsorption of iodine from carbon tetrachloride. The curves for raw Micronex and raw Super Spectra are not in exact agreement with the extracted samples. It is doubtful whether this difference is due to the slow rate at which equilibrium was approached, or whether it represents an actual difference in the state of the surface.

Figure 4 gives the data for methylene blue in water. The mechanical precipitant used in this case was zinc oxide and connection was made for the color removed by this agent. The highest curve represents the behavior of National No. 4 adsorptive carbon. It was pulverized and treated in exactly the same way as the other blacks. It had a very decided lag and the curve may perhaps best be regarded as a minimum curve. The curves do not fit the Freundlich equation and it is probable that there is a considerable lag involved in all measurements. They are therefore to be regarded as qualitative, but serve to place the pigments in a very definite order. There are two very decided shortcomings of the data.

Note—The failure of the somewhat similar experimental work of LeBlanc, Kroger, and Kloz to distinguish differences is rather difficult to explain, especially in view of the large adsorption of water vapor by some of their samples.

One is that they represent the behavior at room temperatures only, whereas we are mostly interested in the behavior at temperatures used in vulcanization. Work is now in progress which is designed to give much more accurate data over a range of temperatures. The second drawback is that the results in these media may have little relation to the behavior in rubber. According to Berl and Wachendorff,[14] the lyophile and lyophobe character of the adsorbent is an important factor in the adsorption. The behavior of the

[14] *Kolloid-Z.*, Special No. (April 1, 1925), p. 36.

adsorbent to the solvent should be known. It therefore appears that the only medium which could be used with assurance is one which would give with each of the blacks identical heats of wetting with rubber. This is a difficult requirement to meet. There is consolation in the fact that the results agree in the two solvents.

MOISTURE CONTENT—The differences in moisture content evidently depend upon the adsorptive capacity. The samples as taken from the container were dried to constant weight in an oven at 105° C. The loss is given in Table VII as per cent of the original weight.

Table VII—Moisture Content of Blacks

BLACK	MOISTURE *Per cent*	FLUCTUATION OF MOISTURE *Per cent*
Charlton	2.90	3.5
Micronex	2.80	3.8
Super Spectra	5.70	6.7
Thermatomic	0.06	0.3
Goodwin	0.08	0.5

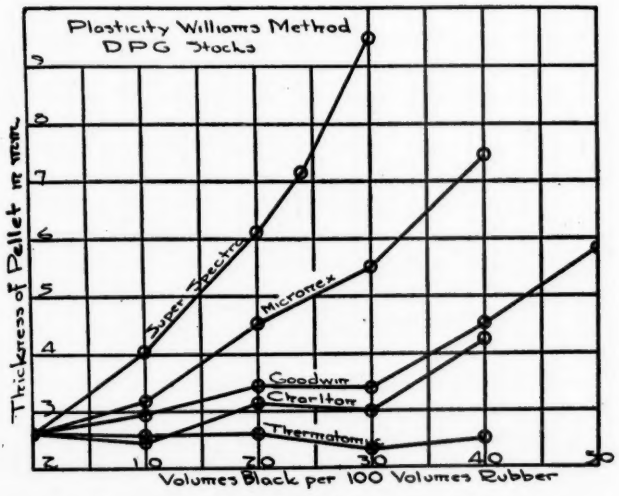

Figure 6

After drying, the sample was placed in the ice box for 24 hours and the gain in weight is given in the second column as per cent on the basis of the dry black.

The anomalous behavior of Charlton appears in several other places and deserves further study. Similar data have been reported by LeBlanc, Kroger, and Kloz[15] with the additional information that benzene or alcohol extraction lowers the adsorptive capacity. This corroborates the differences found in adsorption of dye and iodine by extracted and unextracted samples. These authors attribute the decreased activity to retention of extracting medium. Direct proof of such retention has already been given.

[15] *Kolloidchem. Beihefte*, **30**, 356 (1925).

OIL ABSORPTION—The absorptive capacities are set forth in Table VIII.

Table VIII—Absorptive Capacity

BLACK	OIL NUMBER[a]	WETTING EQUIVALENTS[b]	PETROL[c]	PETROL AND STEARIC ACID[d]	PETROL AND ZINC STEARATE[e]
Charlton	22.0	150	71	75	74
Micronex	18.0	108	60	61	60
Super Spectra	36.0	214	112	117	111
Thermatomic	5.0	36	20	20	20
Goodwin	15.0	114	57	57	56
Kadox Black label		(1)	26.0	23.4	21.0
		(2)	27.7	24.7	22.8
		(3)			21.0

[a] Calculated as cubic centimeters of boiled linseed oil required to bring 10 grams of black to a standard putty-like consistency.

[b] Wetting equivalents as described by Spear and Moore.[13]

[c] Obtained in same manner as preceding column except that a clear mineral oil (petrolatum) was used.

[d] Obtained with same oil as preceding column, but containing 1 gram of stearic acid to 100 cc. of oil.

[e] Obtained with same oil containing 1 gram of zinc stearate per 100 cc. of oil.

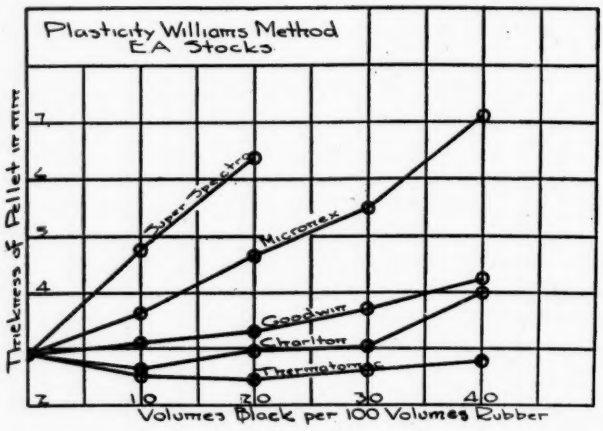

Figure 7

Owing to inherent differences in the blacks and inability to assure exactly similar working, the numerical values in these tables leave much to be desired. The results, however, indicate that within the given limits of oil variation and treatment, the order of behavior is substantially the same, regardless of the materials or personal equation (the results of the last four columns were obtained by a different experimenter).

The addition of stearic acid and zinc stearate is without effect upon the result, and we may fairly deduce that neither has any marked effect upon the dispersion or the flocculating tendency of the blacks in oil. This result checks observations made with the microscope.

The figures for Kadox are rather interesting for, while the differences appear to be just within the experimental error, as estimated by Spear and Moore,[13] the consistency of check runs (1), (2), and (3) indicates that the difference is a real one and that both stearic acid and zinc stearate have a dispersing effect upon the oxide.

SEDIMENTATION—Extensive sedimentation tests were conducted in various media and in the presence of various supposed dispersing agents which should have modified the rate of sedimentation. Some of the single tests have extended over a period of almost two years. It was hoped that particle-size determinations might be made by some variation of the sedimentation method. Consolidation settling took place in all cases,[16] a sharp boundary being formed between the settling black and the clear supernatant material. The rate of fall is entirely independent of the particle size and seems to be a complicated function of the wetting and flocculation of the black. In concentrated suspension the settling gives one the impression of consisting of the shrinkage of one large floc.

Tests in Uncured Rubber

MAXIMUM VOLUME LOADING IN RUBBER—Four hundred grams of smoked sheet were placed upon a 12-inch (30-cm.) mill. After a breakdown period of 5 minutes, carbon was added until the batch either stalled the motor or would not hold together. It was then carefully worked into as smooth a sheet as possible and weighed. The results are given in Table IX.

Table IX—Maximum Volume Loading
(Weight of rubber, 400 grams)

BLACK	WEIGHT OF BLACK	BLACK IN 100 VOLUMES RUBBER	CHARACTER OF MIX
	Grams	*Volumes*	
Charlton	475	67	Smooth
Micronex	456	59.3	Lumpy, rough
Super Spectra	336	41.4	Rough, tough
Thermatomic	1615	154.0	Smooth, leathery
Goodwin	491	62.9	Smooth

The order of increasing loading is the same as the order of increasing particle size. The role of adsorption in this phenomenon is obscure, but it is noteworthy that the oil number and wetting equivalent do not place the blacks in the same order as the maximum volume loading. The explanation may perhaps be found in the preferential adsorption of one or other substance by the blacks. This point must remain undecided until more complete data on adsorption are at hand.

The characteristics of the finished batch are interesting. The conditions of milling of the Micronex and Super Spectra batches were such that we would not expect "scorching," a common phenomenon with gas blacks of this type. The behavior of the batches was nevertheless similar to that of a scorched batch. They could not be worked smooth and the addition of diluting rubber, in all cases tried, resulted in lumpy stock. It seems probable that these cases represent true maximum loading. The other batches rather indicate the limit of the mill to pull the load or the difficulty of keeping the batch on the rolls.

[16] Bancroft, "Applied Colloid Chemistry," 2nd ed., p. 234.

The behavior of Super Spectra and Micronex opens the question of the cause of scorch. This effect is often attributed to oxygen vulcanization. Another possibility is that the rubber becomes mobile enough at the high temperatures to allow excessive flocculation. This question might be the source of some very interesting experimentation.

FURTHER OBSERVATIONS ON MILLING—The time of milling of a given volume of black into a given volume of rubber depends largely upon the state of compression of the black. It is therefore impossible to give exact figures, but the order of increasing milling time is Thermatomic, Charlton, Goodwin, Micronex, Super Spectra. The blacks have characteristic odors during milling and can easily be identified by this means. A study of the outgassed material from these blacks will probably give interesting information concerning the non-carbon materials responsible for the odors.

The mixed batch of Super Spectra was always very tough on the mill and could be greatly distorted while warm without actual flow taking place. This characteristic high resistance to flow makes Super Spectra batches very difficult to

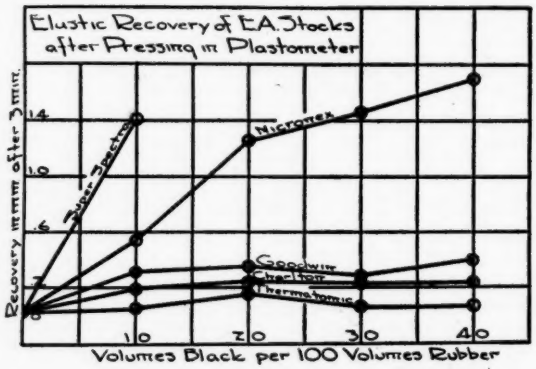

Figure 8

handle on the mill. If the batch is rolled and the mill opened wide, the batch easily passes through without flow, and then retracts almost to its original dimensions. If the mill is tightened the batch will then again squeeze through without flow and this may be repeated several times until the elastic limit of the batch is reached where the mill chokes and the motor stalls. Micronex exhibits the same tendency to a limited extent. The effect increases with the loading of black. The behavior is almost entirely lacking in Charlton and Thermatomic, which become more leathery as the loading increases. Goodwin seems to occupy a middle ground.

SOLUBILITY OF MIXES IN BENZENE—It is well known that certain carbon blacks interfere with the solution of rubber.[15] This effect was studied in the five blacks by milling a series of stocks with various volume loadings and placing small cubes of the stocks in bottles with benzene. In every case

but one there was a limiting volume loading beyond which the stock would not disperse in the solvent. The values are given in Table X.

Table X—Maximum Volume Loading

Black	Volume at Which Solution No Longer Occurred
Charlton	45
Micronex	25
Super Spectra	10
Thermatomic	(154)
Goodwin	32

The end point is not sharp, but the differences are so great as to make the effect very striking. In the case of Thermatomic, at 154 volume, the dispersion was not smooth, but the original lumps were not present in the liquid.

It is believed that this behavior should not be considered as retarded solution, but as complete inhibition of dispersion, for while the total lump does not go into solution, the rubber is extracted from the lump and makes a perfectly clear solution in the surrounding benzene. The writers have samples which have been in this state for 18 months and show no sign of dispersion. If such a sample cube is worked under the spatula until all the solvent disappears, it will present a smooth surface and be apparently free from lumps. A drop of benzene upon this surface causes the film to break and draw up into little lumps, showing that the black rubber structure remains intact. The explanation of this behavior is quite obscure and may depend upon further knowledge of the constitution of the several phases of rubber. It is possible that only the "diffusion rubber" is extractable and the "gel skeleton" material is retained, more or less mechanically.

One of the questions which presented itself was whether some of the rubber really was irreversibly adsorbed, or whether sufficiently long extraction would remove it completely. Benzene extractions of pellets of rubber-black compositions were made on various loadings of Super Spectra and on several of the other blacks. The results are shown graphically in Figure 5.

Curves 1 to 4 are all Super Spectra black at loadings of approximately 15, 20, 30, and 40 volumes of black per 100 volumes of rubber. Benzene extraction apparently brings these stocks together in composition, and after almost 50 days of continuous extraction the rubber content is comparatively high, indicating that complete removal would be a matter of excessively long extraction. Curve 5 represents the behavior of Micronex, which seems to approach a different value from that of Super Spectra as a minimum. Curve 3′ is identical with 3 except that the same stock was milled on a cold mill for 2 additional hours. The milling had no effect within the accuracy of experiment. Curve 7 is identical with 3 but the extraction was carried out with ether instead of benzene. The rate of extraction is much slower. Curve 6 is Goodwin black. The experiment was performed at a

different time and conditions may have been slightly different.

The other blacks were extracted in the same way, but the pellets were not so firm and disintegrated with the agitation attending extraction. The results are therefore of no great value. Black Label Kadox also gives mixes at high loadings which are insoluble. Kadox is the only pigment aside from carbon blacks which, to the writers' knowledge, displays this property.

PLASTICITY OF UNCURED STOCK—Plasticity measurements were made on the diphenylguanidine and E. A. stocks (described in Part II of this paper) while in the uncured state, using the Williams plastometer. The results are shown in Figures 6 and 7, where the thickness of a 2-cc. pellet after 3 minutes' pressure at 70° C. under 5 kg. is plotted as ordinate. The stocks were identical except for the differences in the blacks and the volume loading, which is plotted as abscissa.

It may be seen that the difference in stiffness before cure is in the same order as particle size. A notable feature is that Goodwin and Charlton at 40 volume loadings are no stiffer than Super Spectra at 12 volumes and Micronex at 20. This would indicate that either one of these blacks would be much easier to handle in the factory.

RECOVERY—Parallel to the plasticity results are the measurements of the recovery of the stocks. The pellets were allowed to rest 3 minutes after removal from the plastometer and gaged again. The increase in thickness has been named "elastic recovery" and is plotted in Figure 8. These data also show the difference in stiffness of the various stocks and, together with the plasticity values, may be taken as an indication of the handling on the mill.

BLOOMING OF SULFUR-CONTAINING MIXES IN UNCURED STATE—The blooming of sulfur on uncured stock is materially affected by the black. Stocks containing Super Spectra had practically no tendency to bloom. Micronex stocks bloomed slightly more. The others displayed increasing bloom in the order, Charlton and Goodwin about the same, Thermatomic. It was also quite noticeable that stocks containing mercaptobenzothiazole were much more prone to bloom than those containing other accelerators. This difference in tendency to bloom is explained by H. A. Endres as being due to differences in the hardness of the stocks.[17]

Acknowledgment

The authors are indebted to the Binney & Smith Company, to the Thermatomic Carbon Company, and to the Bihn and Wolfe Company for making available samples of their carbon blacks.

[17] Private communication.

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Carbon Blacks and Their Use in Rubber[1]

II—Experiments in Cured Rubber

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This is the second part of a study of several carbon blacks to determine what characteristics of the black are most largely responsible for imparting to rubber those properties which will make for long life in a tire tread. In Part I the characteristics of the blacks themselves as well as their behavior in uncured rubber were compared. This article discusses their action when compounded in cured rubber stocks containing various accelerators—mercaptobenzothiazole, diphenylguanidine, hexamethylenetetramine, ethylidene-aniline, litharge—and a base mix of rubber and sulfur.

IN ORDER to determine what factors in the physical make-up of a given carbon are most largely responsible for the behavior in rubber which determines its suitability in a tire tread, it is essential that we should know what particular property or properties of rubber are responsible for long life in a tire tread and what measurable characteristics of rubber may be used as an index of the life of the tire tread. It has been variously held that tensile, stiffness, resilient energy, etc., are measures of resistance to abrasion. With such a wide diversity of opinion it would be obviously unwise to lay too much weight on any one property. A study has accordingly been made of a number of properties as developed by the five blacks discussed in Part I[2]—Charlton

[1] Received January 30, 1928.

[2] IND. ENG. CHEM., **20**, 621 (1928).

lampblack, Micronex, Super Spectra, Thermatomic, and Goodwin. The blacks have been compounded in rubber mixings of six different base stocks.

Four organic accelerators—mercaptobenzothiazole, diphenylguanidine, hexamethylenetetramine, and ethylideneaniline—were used and less extensive tests were made with litharge acceleration and a base mix of rubber and sulfur.

Materials Used

The materials used were of a standard grade of purity. All rubber was first-quality smoked sheet which had been previously blended into a large master batch. The sulfur was a high grade of precipitated sulfur. The zinc oxide was a standard grade used by the rubber trade. Stearic acid was clean triple-pressed cake. The four accelerators were commercial samples obtainable on the market and made for the trade. The one designated as ethylidene-aniline was the *A* 19 of the Rubber Service Laboratories, one of the resinous commercial grades of this type of accelerator.

Preparation and Curing of Stock

The methods used throughout were as nearly as possible in conformity with the Report of the Physical Testing Committee of the Division of Rubber Chemistry.[3] The blacks were in all cases milled into large master batches of 44 volumes black per 100 volumes rubber, except in the case of Super Spectra, where 30 volumes was the highest loading compatible with good working.

MILLING—The blended smoked sheet, black master batch, and accelerator master batch were mixed on the mill for 5 minutes, at which time the batch ran smooth. During the next 5 minutes pigment was added, and finally the batch was mixed by rolling and re-rolling for exactly 5 minutes. In the case of mercapto batches 5 minutes were consumed in mixing the stearic acid, which was added just before the pigment. This procedure was used on all batches containing from 500 to 800 grams of rubber, the only deviations being in the case of a few of the 40-volume batches and several of the Super Spectra batches where milling was very difficult.

The mill was run at equilibrium for all batches, and the milling temperature was therefore very high. The litharge and rubber-sulfur mixes were milled on a different mill where this procedure was impossible because of the excessively high equilibrium temperature.

CURING—Milled sheets were allowed to stand for 24 hours exposed to the air and were cured in a 2-mm. engraved four-cavity mold, which enabled the curing under identical conditions of samples which it was desirable to compare. The steam press was regulated by a thermostatic regulator and the steam chamber could be held to temperature within 0.5° C. The actual sheet temperature was not determined

[3] IND. ENG. CHEM., 17, 535 (1925).

and it is the steam-chamber temperature to which reference is made throughout this paper. The cured sheets were allowed to stand between 24 and 48 hours before testing. Where solid pieces of rubber were cured—e. g., abrasion rings—an extra period of 10 minutes was added to the cure to correct for mold lag. These cures are nevertheless recorded as having the same time as the sheet cure; thus the ring recorded as a 30-minute cure was actually cured for 40 minutes.

Mercaptobenzothiazole Stocks

FORMULA—The base formula was chosen to give the correct technical cure in approximately 1 hour at 125° C. with a stock containing 20 volumes of Micronex, and consisted of smoked sheet 100, zinc oxide 5, sulfur 3.50, mercapto 1.25, stearic acid 4.00. The actual time of optimum cure was a little less than 1 hour. Into this base were introduced 10, 20, 30, and 40 volumes of each of the blacks, per 100 volumes of rubber. The times of cure for the Micronex standard stock ranged from 30 minutes to 2 hours. Other stocks were cured over a correspondingly long range.

TIME OF CURE BY PHYSICAL MEASUREMENTS—The time of cure varied greatly with the type of black. The proper technical cure was determined by tearing and general handling of the stock. The optimum time of cure is plotted in Figure 1 and will hereafter be designated as "best cure."

Such a procedure depends upon the judgment, experience, and tradition of the experimenter, and for the benefit of those using other criteria the optimum cure has been chosen in two other ways. In Figure II the optimum tensile has been read from the curve of tensile *vs.* time of cure and plotted against the volume loading. Tensile product has been plotted in the same way. It may be seen that the optimum tensile occurs in general about 10 to 15 minutes later than the optimum tensile product. The latter quantity is in nearest agreement with the estimation by hand methods. The optimum time determined from tensile product is usually slightly longer than that determined by hand, as shown in Table I.

Table I—Times of Cure of Various Stocks

VOLUME LOADING	THERMATOMIC		GOODWIN		MICRONEX		CHARLTON		SUPER SPECTRA	
	Hand	T.P.	Hand	T.P.	Hand	T.P.	Hand	T.P.	Hand	T.P.
	Min.	*Min.*	*Min.*	*Min.*	*Min.*	*Min.*	*Min.*	*Min.*	*Min.*	*Min.*
0	20	30	20	30	20	30	20	30	20	30
10	20	18	20	30	30	65	30	50	60	65
20	20	20	20	30	45	55	45	40		
30	20	10	20	25	45	40	45	35		
40	20	10	20	35	45	50	45	37		

The values in the table have been rounded off to even 5 minutes, which is the limit of any observer to judge similar states of cure in such widely differing stocks. The most remarkable feature of the table is the apparent effect of Thermatomic in speeding up the cure. This effect has previously

been noted by Twiss and Murphy.[4] This property of Thermatomic finds a parallel in the tendency of Micronex and Charlton to have the greatest retarding effect at 10 to 20 volumes. It should be noted in passing that the rate of sulfur combination is retarded rather than accelerated by Thermatomic black.

TENSILE—All stress-strain data were obtained by the use of a Scott tensile tester using 1/4-inch (6-mm.) dumb-bell test pieces. The machine was improved in such a way that a single observer could obtain a complete stress-strain chart drawn directly on plotting paper by the machine, with more

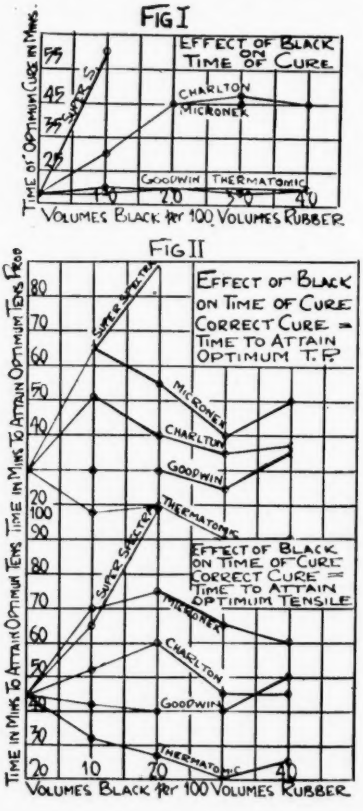


FIG I
EFFECT OF BLACK ON TIME OF CURE
CHARLTON
MICRONEX
GOODWIN
THERMATOMIC
TIME OF OPTIMUM CURE IN MINS.
VOLUMES BLACK PER 100 VOLUMES RUBBER
FIG II
EFFECT OF BLACK ON TIME OF CURE
CORRECT CURE = TIME TO ATTAIN OPTIMUM T.F.
SUPER SPECTRA
MICRONEX
CHARLTON
GOODWIN
THERMATOMIC
EFFECT OF BLACK ON TIME OF CURE
CORRECT CURE = TIME TO ATTAIN OPTIMUM TENSILE
TIME IN MINS TO ATTAIN OPTIMUM TENS. TIME IN MINS TO ATTAIN OPTIMUM TENS. F.F.
VOLUMES BLACK PER 100 VOLUMES RUBBER

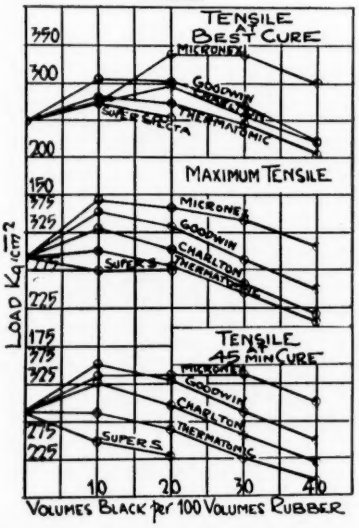
exact results than those obtained by the two-observer method. The tensile strength developed by the different blacks varies over a wide range, as may be seen in Figure III. The tensile has been plotted at three points taken from the tensile–time of cure curve. It may be seen that, regardless of how the blacks are compared, the result is the same. The tensile developed by Micronex is highest and does not fall off so rapidly as the other blacks with increase in the loading. Goodwin

[4] *J. Soc. Chem. Ind.*, **19**, 121T (1926).

is second, Charlton third, Thermatomic fourth, and Super Spectra fifth. This result was not to be expected on the basis of the rather generally accepted hypothesis that tensile is more or less connected with particle size. The most finely divided black has the lowest tensile. It is evident that if particle size is an important factor it has been completely masked by another effect. This point will be taken up again later.

It has been mentioned in the literature that channel black has an unusual ability to retain a high tensile, not dropping appreciably below the base mix in tensile until over 40 volumes of black have been added.[5] The present data show that the maximum tensile of Micronex reaches a high value at about 10, rather than 25, volumes and decreases constantly from that point. This small difference is perhaps traceable to the difference in the choice of base mix.

FIG III



TENSILE PRODUCT—The effect of the blacks upon the tensile product of the mix is similar to that upon the tensile. Again Micronex is superior to the other blacks. The general tendency seems to be to reach a maximum at 10 volumes and to decrease rather rapidly thereafter. Thermatomic does not go through a maximum, but begins to fall off at once. Goodwin falls off more rapidly after 10 volumes than any of the others and occupies the lowest position at 40 volumes.

RESILIENT ENERGY—These values were obtained by measuring the area under the stress-strain curve with a plantimeter. The values were plotted against the time of cure. From these curves were taken the values at best cure, maximum, and at 45 minutes, which are plotted in the curves

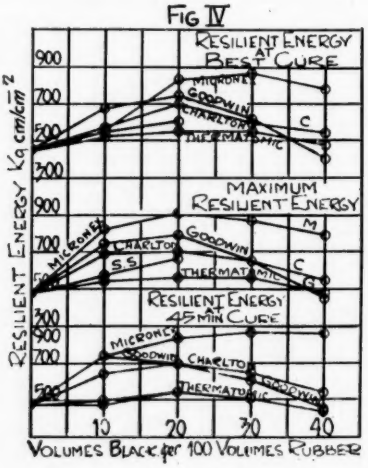
[5] Weigand, *Can. Chem. J.*, **4**, 160 (1920).

shown in Figure IV. The resilient-energy curves are somewhat flatter than the tensile or tensile-product curves, because the stress-strain curve more nearly approaches Hooke's law as the volume loading increases. The relative positions of the curves are about the same and the tendency of Goodwin to fall off somewhat faster than the others is again apparent.

MODULUS—The values for modulus of the various stocks at 300 and 500 per cent are shown in Figures V and VI. Although the values are plotted in three different ways, the results are identical. In this case, as in the case of tensile, the measured values have no relation whatever to particle size. The curves are also in a totally different order than the tensile, tensile-product, or resilient-energy results.

HARDNESS—It was very quickly recognized that, although stock containing Goodwin black was high in modulus, it was soft and resilient when flexed in the hand. The resistance of a stock to high deformation is ordinarily known as

FIG IV



stiffness or modulus, and will be so designated hereafter. The resistance to low deformation is usually known as hardness. It becomes evident from an examination of Figures VII and VIII that hardness is not related to modulus when comparing stocks containing different pigments. The difference in shapes of the stress-strain curves in Figure XXXI will make the relation somewhat clearer. Hardness shown in Figure VII was determined by means of the Shore durometer, that in Figure VIII was determined in the Goodyear Laboratories by means of a pendulum similar to that mentioned by Healy.[6] (Hardness is the reciprocal of the depth of penetration of the impact point.)

The hardness of finished vulcanized stock places the blacks in the same order in which they are placed by the plasticity

[6] *Rubber Age*, **5**, 621 (1925).

FIG V

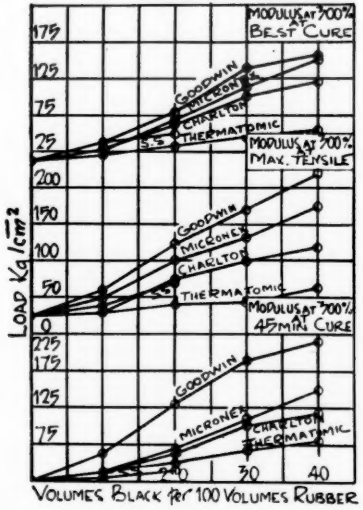


FIG VI

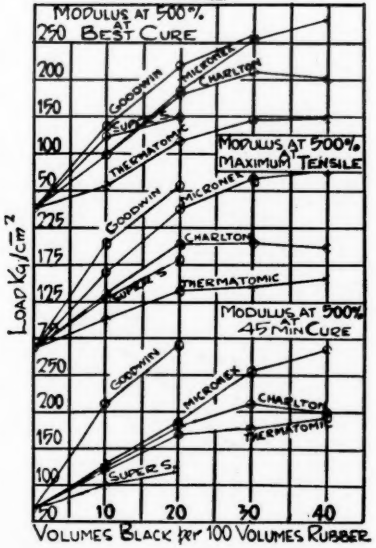


FIG VII

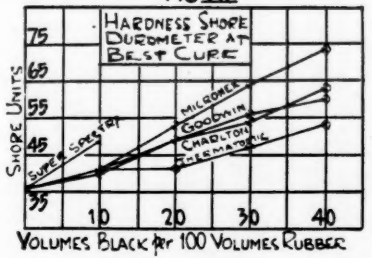
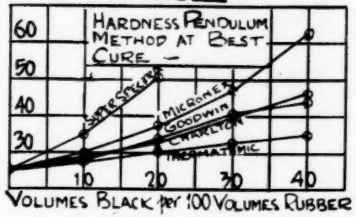


FIG VIII



of the stocks unvulcanized. This order is the same as that of the estimated particle size.

It seems probable that both plasticity and hardness depend upon the forces of flocculation of the pigments. If we assume that the character of the surface is the same for all blacks, then the hardness of a stock is probably a function of particle size, since increasing fineness increases the total surface effect of a given mass of pigment. The order of hardness of the stocks is in complete agreement with this view, and we may predict for further cases that, in a rubber medium of a given hardness, the hardness of the stock will increase with increasing fineness of division of the black.

The question immediately arises why this "reënforcing effect" at low elongation does not persist at higher elongations. In other words, why is not modulus also a function of particle size? It seems probable that this anomalous behavior may be due to the effect of the surface of the black upon the vulcanizing agents rather than on the rubber medium. A highly adsorptive carbon removes the curing agents from the rubber to such an extent that it is for practical purposes impossible to get a satisfactory rubber gel upon vulcanization. The adsorptive capacity of a carbon black is thus probably exhibited in several ways: (*a*) by its effect in determining the flocculating tendency of the pigment, which in turn determines the yield properties and mobility of the resulting mix; and (*b*) by its effect in removing the curing substances responsible for gel formation.[7] Assuming again that all carbon-black surfaces are of the same type, we may imagine certain representative cases:

(*a*) Large particle size, small amount of surface, low adsorptive capacity, little flocculating tendency, soft before cure, soft after cure, fast curing, well-gelled matrix, low modulus and low permanent set, high recovery from deformation.

(*b*) Medium particle size, medium amount of surface, rather low adsorptive capacity, rather small flocculating tendency, medium soft before cure, medium soft after cure, fairly fast curing, well-gelled matrix, high modulus and rather low set.

(*c*) Exceedingly small particle size, exceedingly large surface, exceedingly high adsorptive capacity, great flocculating tendency, hard before cure, hard after cure, slow curing, poorly gelled matrix, low modulus, high permanent set and flow upon deformation.

If this assumption of a single type of surface for all carbon black represents the actual state of affairs, the matter of selecting and preparing an ideal black is only one of striking a happy medium. If, on the other hand, the surfaces of different blacks differ in quality as well as in quantity, we may hope to prepare a black which (*a*) is finely divided, (*b*) does not produce an unmanageable stock when milled, and (*c*) does not interfere with the gelling of the rubber; thus combining the desirable features of the several cases listed above in a rather larger degree than we could otherwise expect. The success to be attained with such a type

[7] Compare Rhodes and Goldsmith, IND. ENG. CHEM., **18**, 566 (1926).

Table II—Effect of Addition of Stearic Acid on Resistance to Abrasion

Stock	Cure (125° C.)	Modulus 300 %	Modulus 500 %	Modulus 700 %	Tensile	Elongation	Tensile Product	Resilient Energy	Shore Hardness	Abrasion Loss	Energy Loss
	Min.				*Kg./cm.²*	*Per cent*		*Kg./cm./cm.²*		*Cc.*	*Per cent*
Base	15	10	24	85	212	860	182	374	35	4.0	
	20	15	35	165	265	800	212	453	35	4.1	
	30	18	45	195	280	780	218	488	36	3.7	12.2
	45	25	67	265	290	725	210	477	38	3.1	
Base without stearic	15	10	23	83	245	840	206	430	31	7.4	
	20	11	28	118	257	820	210	480	32	7.1	
	30	14	35	137	270	810	218	486	32	6.4	13.4
	45	16	40	160	275	795	219	494	34	7.0	
20 vol. Charlton stearic	60	75	207		302	620	187	667	51	1.8	21
No stearic	60	55	155		290	690	290	689	46	3.3	22
20 vol. Micronex stearic	60	84	220		355	670	238	884	57	1.7	37
No stearic	60	56	147		230	640	147	512	50	4.1	37[a]
20 vol. Thermatomic stearic	15	28	97		262	720	189	535	40	3.5	15[b]
No stearic	15	32	107		282	720	203	583	44?	5.3	13[b]
20 vol. Goodwin stearic	20	82	225		302	620	187	700	49	2.1	29[b]
No stearic	20	62	184		245	590	145	502	47	3.3	31[b]

[a] 75-minute cure.
[b] 30-minute cure.

of carbon would depend upon the degree to which resistance to abrasion is a function of particle size per se and how much a function of flocculation.

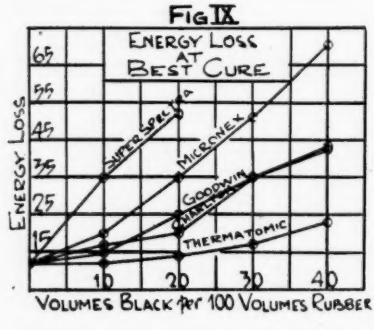
Table III—Plasticity of Rubber-Black Mixes with and without Zinc Stearate

	Plasticity	
	With Zinc Stearate	Control
5 zinc stearate per 100 rubber 34 volumes black per 100 volumes rubber	7.35	6.82
3.7 zinc stearate per 100 rubber 21 volumes black per 100 volumes rubber	4.43	4.47

Table IV—Physical Data—Litharge Stocks

Time of Cure (142° C.)	Modulus 300%	Modulus 500%	Tensile	Elongation	Tensile Product	Volume Loss on Abrasion	State of Cure
Min.			*Kg./cm.²*	%		*Cc.*	
			CHARLTON				
20	30	85	170	665	113		
30	40	120	220	580	150	5.90	
45	45	125	235	675	169		Best
60	50	135	240	660	159	4.56	
90	55	135	215	625	135	4.70	
120	57	140	200	610	122	4.21	
180						4.70	
			MICRONEX				
30	60	415	220	570	125	5.46	
45	65	150	220	570	125		Best
60	70	160	225	570	128	4.75	
90	80	165	190	500	95	4.63	
120	80		175	475	83	4.48	
180						4.18	
			THERMATOMIC				
15	22	67	205	720	148	7.73	
20	25	75	215	720	155		Best
30	27	90	230	725	167	7.60	
45	30	95	240	725	174		
60	30	100	210	680	143	7.16	
90						8.13	
			GOODWIN				
15	65	180	220	575	126	4.36	
20	75	190	235	575	135		Best
30	80	210	245	550	135	4.01	
45	90	215	235	535	126		
60	95	220	220	500	110	3.22	
90	100		180	410	74		
120						3.14	

The whole issue is somewhat befogged by the fact that the rubber is undoubtedly more severely broken down when milling a very fine pigment than when milling a coarser one. This certainly affects the rigidity of the gel obtained upon vulcanization.



Energy Loss—This quantity was determined by the height of rebound of the impact pendulum mentioned above. The data are plotted in Figure IX, as per cent of total energy input which is lost.

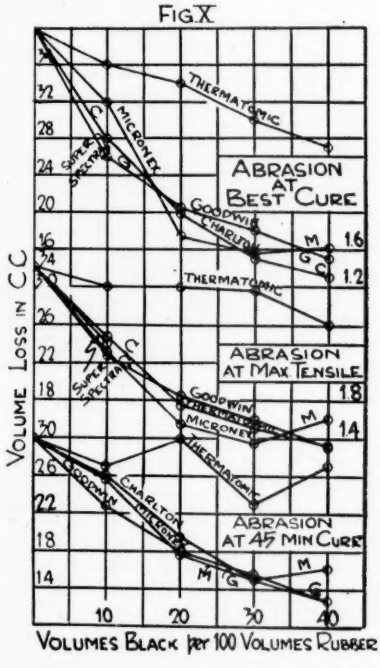
Resistance to Abrasion—Abrasive wear was studied with the abrasion machine furnished by the Akron Standard Mold

Company. The machine consists essentially of an alundum grinding wheel which is driven by a rubber test ring running at an angle against the periphery of the abrasive wheel. The abrasive wheel is thrust against the rubber ring by means of a weight (2.5 kg. in these tests) acting through a balance system. The angle may be set as desired and 40 degrees was used in all tests. The bronze bearing in which the abrasive wheel runs was found rather unsatisfactory and was replaced by ball bearings. Several other changes were made in the machine during the latter part of the tests. The litharge and rubber-sulfur stocks were run on the improved machine.

The surface of the wheel was kept free from buffings by a stream of air. A brush is not satisfactory.

The abrasion results are shown in Figure X. They serve very definitely to separate Thermatomic from the other blacks. The other curves cross to such an extent that the experimental method does not distinguish between them. The inferiority of Thermatomic is also definitely shown in Figure XI. Charlton, Micronex, Thermatomic, and Goodwin are labeled 3, 4, 5, and 6, respectively. Differences in grain of the abraded surface are due in part to cure, all rings being cured 45 minutes at 125° C.

FIG. X



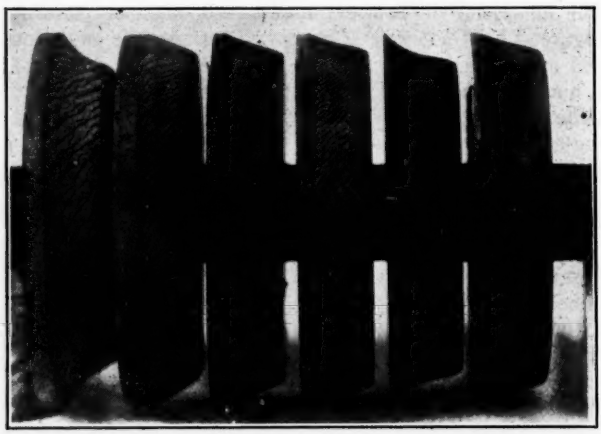
The most important information obtained from Figure X is that the resistance of all these stocks to abrasion continues to increase with volume loading beyond the point of maximum-tensile or maximum-resilient energy.

It must not be assumed that the abrasion data presented here and later are indicative of road wear. Undoubtedly they are in some cases; in others it is quite certain that they are not. On the other hand, the test does measure a definite physical characteristic of rubber and as such is worthy of study. The fact that increased volume loading up to 35 volumes increases the resistance to abrasion has been checked by actual tire tests in the case of one of the blacks.

It is evident from these results that there is no relation

between resistance to abrasion and resilient energy. These abrasion results are in complete disagreement with the optimum loading as found by Weigand[6] and also with the results obtained by Greider.[8] At present we have no explanation for the discrepancy.

Effect of Stearic Acid on Modulus-Cure Curve—Stearic acid has a remarkable effect upon mixes containing mercaptobenzothiazole. Sebrell and Vogt[9] have shown that, in the entire absence of fatty acid or a similar activating agent, mercaptobenzothiazole is practically inactive. Rubber ordinarily contains enough such material to produce a good cure in an unloaded stock. In the presence of carbon black of the channel type, a larger amount of acid must be present to produce a satisfactory vulcanizate. It behaves as if the stearic acid were removed from the field of action, although the effect is probably more complex. The effect of additional stearic acid upon the stress-strain curves of a mercapto-



1 2 3 4 5 6

Figure XI—Comparative Abrasive Wear of Tire-Tread Stocks

benzothiazole stock containing 20 volumes of channel black is shown in Figure XII. The figures on the curves, 20, 45, and 90, represent the cure of the stock without stearic acid; 20*A*, 45*A*, and 90*A* are the identical cures for the same stock with the addition of 4 parts of stearic acid per 100 parts of rubber. It may be seen that the stress-strain curves are raised by the addition of stearic acid, that the tensile is increased, and that the curves are separated and spread over a greater range. The same effects may be seen in the second group of curves in Figure XII, where a stock containing 20 volumes of Super Spectra has additions of 4 parts for the curves marked *A* and 12 parts for the curves marked *B*. It was determined by a complete set of experiments that the improvement could

[8] Ind. Eng. Chem., **15**, 504 (1923).

[9] *Ibid.*, **16**, 792 (1924).

not be obtained by increase in any of the other active agents. The same results are obtained with Goodwin except that the improvement is by no means so marked as in the cases of Micronex and Super Spectra.

In the case of unloaded stocks or of stocks loaded with non-adsorptive pigments, the increase in tensile strength is absent or very slight, but a marked spreading of the stress-strain curves takes place as shown in Figure XII. The 10-minute cure for the stock without stearic acid is higher than the corresponding cure with the acid. The converse is true of the 45-minute cures. The same relations exist in the curves for stock containing Thermatomic. Charlton black behaves somewhat more like Micronex than Goodwin, although the improvement in tensile strength is much less.

The most noticeable effect of stearic acid in the stocks here studied has also been noticed in high zinc oxide loadings and may be described as a steepening of the modulus–time of cure curve. The addition of oleic acid to a litharge accelerated tube stock has been observed to give the same effect. Sebrell and Vogt[9] have shown this effect for most organic accelerators.

Effect of Stearic Acid upon Abrasion—One of the most notable results of the addition of stearic acid is the improved resistance to abrasion. (Table II)

A comparison of the 20-minute cure of the base stock with the 45-minute cure of the base stock without stearic acid shows that the stress-strain curves are nearly identical. The resistance to abrasion, however, differs by 75 per cent, the base stock being superior. In Figure XI ring 2 is the base stock and ring 1 the base stock without stearic acid. An example may also be seen in the case of the Thermatomic stocks (Table II), where practically identical stress-strain behaviors give widely different abrasion resistances.

The explanations of these various phenomena which have been proposed previous to this time do not seem to be altogether satisfactory. The effect of stearic acid upon carbon-black stocks has been accounted for by the supposedly improved dispersion of the black. If the black were more completely dispersed, the resulting stock should be softer according to the observations of Green.[10] A small effect of this kind is observed in all uncured stock and in cured stock where no zinc oxide is present, as in a rubber-sulfur mix. Zinc oxide is generally used in such quantity that the free acids are probably removed to a large extent during cure. When no zinc oxide is used in a stock, the addition of any fatty acid always results adversely—e. g., in a rubber-sulfur mix. It therefore seems probable that free fatty acid is not responsible for the improvement.

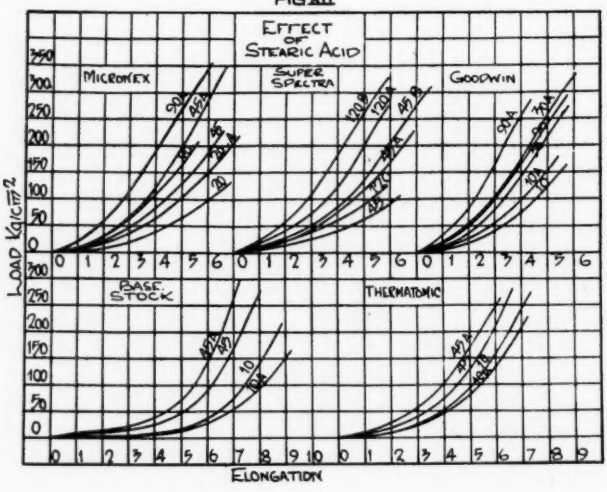
It has been further suggested that the zinc soaps are the real dispersing agents. This must also be rejected in view

[10] Ind. Eng. Chem., **15**, 122 (1923).

of the fact that better dispersion should give a softer stock. The work of Arsem[11] seems to indicate that the zinc soaps are gelling rather than dispersing agents. Perrott[12] says: "Small amounts of metal soaps in a thin varnish tend to cause agglomeration even in long blacks." The present writers' experiments upon wetting equivalents[2] indicate that zinc stearate is without material effect upon the black dispersion in mineral oil. The plasticity of uncured black stocks does not seem to be materially affected by the presence of zinc stearate, as shown by Table III.

The milling treatments were as nearly identical as it is possible to make them. From these varied facts it is concluded that the improvement is not due to improved dispersion of the black by zinc stearate. If zinc stearate has any effect whatever on the black, it is to decrease the wetting of the black

FIG XII



by the medium and hence cause its flocculation which would presumably partly account for the improvement. It is the writers' opinion, however, that most of the results must be explained in some other way.

The differences in stocks with and without stearic acid never appear before cure. These differences, although enhanced by the presence of carbon, are nevertheless observed in cases where pigmentation is kept at a minimum. The quality of practically all stocks where organic accelerators are used is dependent upon the presence of zinc oxide and fatty acids in reasonable quantity. Fatty acids are also necessary in the case of litharge acceleration. The use of zinc oxide and fatty acid improves the quality of a rubber-sulfur mix. It seems, therefore, that these phenomena are not closely

[11] IND. ENG. CHEM., **18**, 157 (1926).

[12] Neal and Perrott, Bur. Mines, *Bull.* **192** (1922).

related to the degree of dispersion of carbon black, but are largely due to the effect of soap-forming substances upon the rubber gel.[13]

Sufficient data are not at hand to venture a detailed explanation but it seems possible that these phenomena may stand in close relation to the gelation of paints by zinc soaps described by Arsem.[11] A further fact of interest is that zinc stearate will form a gelatinous precipitate in mineral oil.

Work on this problem is being continued in the hope that we may throw some further light on the role of these ingredients in vulcanization.

Ethylidene-Aniline Stocks

The base formula used was as follows: smoked sheet 100, zinc oxide 5, sulfur 3.5, *A*19 1.25.

Into this base mix 10, 20, 30, and 40 volumes of black were introduced per 100 volumes of rubber, as in the case of the mercapto stocks. The formula was designed to cure in about 1 hour at 142° C. when containing 20 volumes of Micronex. The only variation in procedure of preparation for cure was in the milling time, which was cut to 15 minutes for a batch containing 500 grams of rubber. This was due to the absence of stearic acid.

Time of Cure—The times of optimum cure are plotted in Figure XIII. The hand judgment of cure checks the maximum tensile results in regard to the order of curing rate. The optimum time of cure is uniformly 20 minutes later than the optimum time as determined by hand tests. The apparent accelerating effect of Thermatomic is again evident and the retarding action of Charlton is even more pronounced than in the case of mercapto.

Tensile—The comparative tensile strengths of the blacks are shown in Figure XIV. Goodwin is unquestionably superior to the other blacks with this accelerator. Even Thermatomic compares very favorably with Micronex. Micronex and especially Super Spectra interfered with the cure more with this accelerator than with the mercapto.

Tensile Product—The tensile product relations are shown in Figure XV. It is rather surprising to find Thermatomic so definitely superior in this property. Goodwin in a general way seems to rank second, although not very far above Charlton and Micronex.

Resilient Energy—These values are shown in Figure XVI. It may be seen that Goodwin is best on the average and Thermatomic second. The difference between this result and the tensile-product result is, of course, due to the straighter stress-strain curve of Goodwin. Micronex and Super Spectra are definitely poorer.

Modulus—The modulus at 500 per cent is shown in Figure XVII. These results are quite close to those obtained with

[13] See also Whitby and Cambron, *J. Soc. Chem. Ind.*, **42**, 333 (1923). The explanation given is different.

FIG XIII

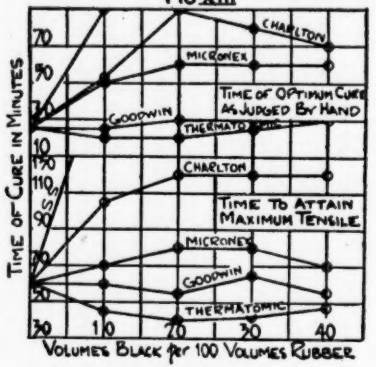


FIG XIV

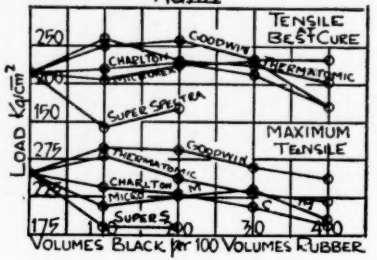


FIG XV

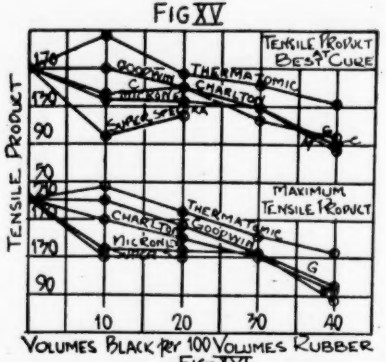


FIG XVI

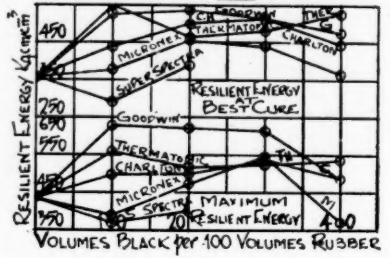


FIG XVII

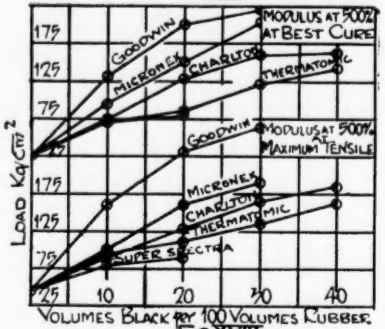
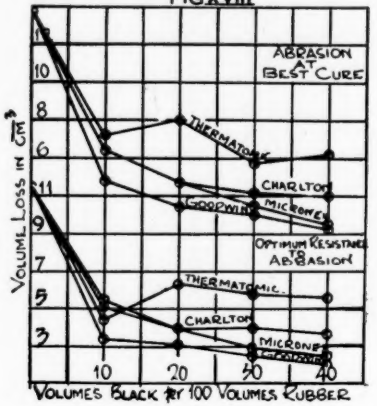


FIG XVIII



mercapto except that Super Spectra is less stiff. As previously mentioned, this accelerator seems much more affected by Super Spectra than mercapto.

HARDNESS—The hardness is in close agreement with the results on the mercapto stock, indicating that the state of the rubber matrix has less effect upon this property than most of the other physical quantities measured.

RESISTANCE TO ABRASION—The resistance to abrasion, shown in Figure XVIII, indicates that Goodwin black is superior to any of the others, with Micronex a fair second. It may be seen at a glance that abrasion places the stocks in an order not to be predicted from any of the other quantities measured, with the exception of modulus. Especially noteworthy is the inferiority of Thermatomic, considering its comparatively high tensile and resilient energy.

Hexamethylenetetramine Stocks

The base formula was smoked sheet 100, zinc oxide 5, sulfur 3.5, hexa 1.75. As in previous cases, 10, 20, 30, and 40 volumes of each black per 100 volumes of rubber were introduced into this mix, and the formula was designed to cure in about 1 hour when containing 20 volumes of Micronex. The temperature of cure was 142° C.

Milling, curing, and testing procedures were identical with those used for E. A. (ethylidine-aniline) stocks.

TIME OF CURE—The times of optimum cure are plotted in Figure XIX. The retardation of cure is less than in the case of E. A. stocks. The apparent accelerating effect of Thermatomic is even more apparent here than in the preceding cases. Goodwin also seems to cure slightly faster. Even Micronex by the maximum tensile-product criterion seems to accelerate the cure, although hand examination of the tearing qualities does not bear this out. However, hexa is less sensitive to the adsorptive blacks than the other accelerators tried.

PHYSICAL CHARACTERISTICS—The tensile, resilient energy, and modulus are shown in Figures XX, XXI, and XXII, respectively, and may be passed as self-explanatory.

ABRASION—The resistance to abrasion (Figure XXIII) places Micronex and Goodwin equal and considerably ahead of the others.

Diphenylguanidine Stocks

The base formula was smoked sheet 100, zinc oxide 5, sulfur 3.5, diphenylguanidine 1.25. The procedure was identical with that used in the case of hexa and E. A.

PHYSICAL TESTS—The results of physical tests are given in Figures XXIV to XXX, and include no novel features except that one stock is given with a loading of 50 volumes. The abrasion results are the result of fewer and less satisfactory tests than in the previous case, but seem to be fairly concordant.

Litharge Stocks

The base formula was as follows: smoked sheet 100, zinc oxide 5, litharge 6, sulfur 4. Stocks were made up at the 20-volume loading only. The tensile and abrasion results are given in Table IV.

It is evident from this table, as from most of the material previously presented, that the resistance to abrasion as here measured does not parallel any of the other physical quantities. The differences in abrasion among the blacks are more pronounced than the differences in tensile strength. Perhaps the most interesting thing about the table is that the abrasion resistance is in approximate inverse proportion to the tensile product.

Another point of interest is that all blacks cure at the same rate as judged by the tensile properties. The tearing properties and general feeling of the stock did not seem to bear this out and the impression of state of cure is indicated in the last column.

EFFECT OF STEARIC ACID—The effect of stearic acid upon this mix is best brought out by Super Spectra. Twenty volumes of black were used; in one case with no stearic acid, in the other with 10 parts to 100 of rubber. The results are shown in Table V.

Table V—Effect of Stearic Acid on Litharge Stocks

Time of Cure (141° C.)	Modulus 300%	Modulus 500%	Tensile	Elongation	Tensile Product	Volume Loss on Abrasion
Min.			*Kg./cm.²*	%		*Cc.*
			NO STEARIC ACID			
30	45	125	140	545	77	
45	55	140	150	525	79	
60	66	145	155	520	81	7.86
90	70	150	160	515	83	7.25
120	75		150	480	72	6.90
180						5.40
240						5.70
			10 PARTS STEARIC ACID			
20	35	110	210	690	145	
30	75	195	280	650	182	2.39
45	90	220	290	610	177	2.28
60	95	225	280	575	161	2.26
90	95	225	225	510	115	2.36
120	100		165	420	70	2.32

The introduction of stearic acid in this mix changed the Super Spectra stock from one of the very poorest in both tensile and abrasion properties to an undoubted best. The action in this case is probably similar to the behavior in the presence of zinc oxide and mercaptobenzothiazole.

STRESS-STRAIN CURVE AT LOW ELONGATIONS—The adjustments on the stress-strain machine were changed so that the elongation of a test piece 4 inches (10 cm.) long could be measured. The rate of stretching (not jaw separation) was the same as for the regular test. Accurate expanded curves were obtained up to 200 per cent elongation. The curves for the 30-minute cures are shown in Figure XXXI. S. S. 1 is the Super Spectra stock without stearic; S. S. 2 is the stock with 10 parts stearic. The other blacks are designated

by the initials. This shows quite clearly and accurately why a stock may have a very high modulus and a very low hardness.[14]

Rubber-Sulfur Mix

The base formula used is smoked sheet 100 and sulfur 10. Stocks were made at the 20-volume loading only. Results of tensile and abrasion tests are given in Table VI.

Table VI—Physical Data—Rubber-Sulfur Stocks

Time of Cure (148° C.)	Modulus 300%	Modulus 500%	Tensile	Elongation	Tensile Product	Volume Loss on Abrasion	Hardness
Min.			*Kg./cm.²*	*%*		*Cc.*	
			CHARLTON BLACK				
30	10	30	80	740	59	Too soft	37
45	15	45	100	730	73	Too soft	40
60	20	55	120	775	87	5.50	45
90	27	67	145	770	105	5.57	49
120	35	87	170	700	119	4.35	49
180	57	125	205	670	137	5.26	56
240	67	135	140	500	70	2.98	61
			MICRONEX				
30	15	55	85	575	49	6.55	51
45	25	70	125	620	78	4.50	58
60	32	95	170	640	109	4.35	60
90	45	137	240	665	160	3.14	64
120	60	170	270	650	175	3.26	66
180	92		210	475	100	2.16?	75
240						2.86	75
			THERMATOMIC BLACK				
30	7	22	100	845	85	10.50	39
45	10	30	140	850	119	10.70	43
60	15	40	160	835	135	9.90	47
90	27	50	190	775	147	9.30	47
120	35	85	170	680	115	11.00	48
180						12.20	
			GOODWIN BLACK				
30	25	75	110	590	65	4.35	45
45	42	125	170	600	102	4.10	52
60	55	150	205	600	123	3.20	58
90	85	205	250	575	144	3.30	60
120	120	255	280	545	153		
180			160	290		3.30	66
240						3.30	69

It is probably a reasonable view, since these mixes are extremely simple, have a high sulfur content, and the base mix is so soft, that the differences in the properties of the blacks themselves are accentuated. Micronex is probably to be chosen as first with Goodwin a very close second as regards abrasion resistance and tensile.

Effect of Stearic Acid—As in several of the preceding cases, Super Spectra at 20 volumes was chosen as the experimental stock. The stock was varied by (*a*) adding 10 parts stearic acid per 100 rubber, (*b*) adding 5 parts ZnO per 100 rubber, (*c*) adding both 10 parts stearic acid and 5 parts of zinc oxide. The results are shown in Table VII.

The stocks were very difficult to handle in every way, but the stress-strain curves tend to corroborate all previous experiments involving stearic acid and zinc oxide. The most striking thing in the table, however, is the result on

[14] See also Le Blanc, Krözer, and Kloz, *Kolloidchem. Beihefte*, **20**, 356 (1925).

abrasion resistance of the stock to which has been added stearic acid alone. The abrasion resistance is enormously better than the standard stock. The feel of the abrasion wheel led to the suspicion that the action here may be solely that of a lubricant which prevents the abrasion wheel from grasping the rubber. The general trend and the great superiority of the last stock in the table are in agreement with the ideas proposed as to the gelation of zinc stearate. The possibility that some of the results are influenced by the purely mechanical factor of lubrication by excess stearic acid makes them doubtful and opens another avenue of experimentation on abrasion.

Table VII—Effect of Stearic Acid and ZnO on Super Spectra Mix

Time of Cure (148° C.)	Modulus 300%	Modulus 500%	Tensile	Elongation	Volume Loss on Abrasion	Hardness
Min.			*Kg./cm.²*	*%*	*Cc.*	
			SUPER SPECTRA			
30	27	70	120	645	7.60	70
45	32	95	155	625	6.00	72
60	35	110	170	610	5.35	75
90	50	130	185	570	4.00	78
120	60	130	185	570	3.90	82
180	100		165	430	3.40	87
			SUPER SPECTRA AND 10 PARTS STEARIC PER 100 RUBBER			
30						
45	25	60	60	500	3.70	68
60	30	75	85	525	2.55	71
90	37	90	120	570	1.90	75
120	40	100	120	570	1.90	
180			110	420		82
240					1.65	83
			SUPER SPECTRA AND 5 PARTS ZNO PER 100 RUBBER			
30	35	100	112	545	6.95	72
45	45	120	137	545	6.00	74
60	50	130	155	550	4.10	78
90	70	155	190	545	3.90	78
120	70	165	200	540		
180	100	210	210	500	3.50	
			SUPER SPECTRA PLUS 10 PARTS STEARIC ACID AND 5 PARTS ZNO			
30	50	137	175	570	2.70	80
45	85	190	215	540	1.45	82
60	95	210	220	510	1.35	83
90					1.26	84
120	100		155	400		
180	130		120	310	1.12	84

Retardation of Cure

The rate of cure of all stocks seems to be in line with the adsorptive capacities of the blacks except for the case of Charlton. Even in this case the oil adsorption and affinity for moisture place the black in approximately the proper position.

The reason for its anomalous behavior is not clear and an explanation of this deviation from the result of the adsorption tests was early sought. A canvass of the situation presented the following possible solutions:

1—The high acetone extract of Charlton black may contain an active retarding agent.

2—The slope of the temperature-adsorption curves of the various blacks may not be the same and Charlton at high tem-

peratures may have an adsorptive capacity equal to or greater than Micronex.

3—The adsorptive equilibrium may be so different in different media that Charlton appears inactive toward dye, etc., in water and carbon tetrachloride, because of its activity toward the media. In rubber it may be very active because of comparatively small activity toward the rubber itself. Some basis for this argument may perhaps be found in the high oil number and high moisture absorption on the one hand, and on the other in the possibility of making high volume loadings in rubber and its low affinity for rubber as measured by the amount held upon benzene extraction.

The first of these possibilities has been investigated. The carbon black was exhaustively extracted with acetone over a period of 3 or 4 weeks until a small sample showed practically no coloration of the extracting medium after several hours' extraction. The black was also wet with water several times during the period of extraction. Upon drying at 105° C. the product was hard and lumpy and not promising as a material for dispersing in rubber. There was little hope of securing a proper dispersion in view of the apparently universal impression that carbon black once wet with water cannot be dispersed. The master batch milled from the extracted black was as smooth as that milled from the raw black. Test batches were made up containing 20 volumes of black. One batch contained the raw black. The second batch contained the extracted sample. The third batch was made from the extracted sample and a quantity of oil was added which was just equivalent to the extractable matter in the original black. The actual amount of black was identical in the three cases. The formulas are given in Table VIII and the results of tests on these stocks in Table IX.

Table VIII—Formulas for Acetone Extracts of Charlton Black

	Raw Black	Extracted Black	Extracted Black and Oil
Smoked sheet	100	100	100
Carbon black	35.6	34.0	34.0
ZnO	5	5.0	5
Sulfur	3.5	3.5	3.5
Diphenylguanidine	1.25	1.25	1.25
Oil			1.60

These data seem rather conclusive in their indication that the extractable matter acts, not as a retarder of vulcanization, but rather as a softener similar to oil. Data of a similar nature on other samples of black support this view.

The second possibility mentioned above is now being thoroughly studied and work on the third will be taken up as soon as results on present work justify it.

Discussion and Conclusions

Comparison of Blacks—The differences in properties of carbon blacks evidently depend upon their mode of preparation, since black from a given process is always easily distinguishable from the product of any other process. The following characteristics probably contribute to the patent

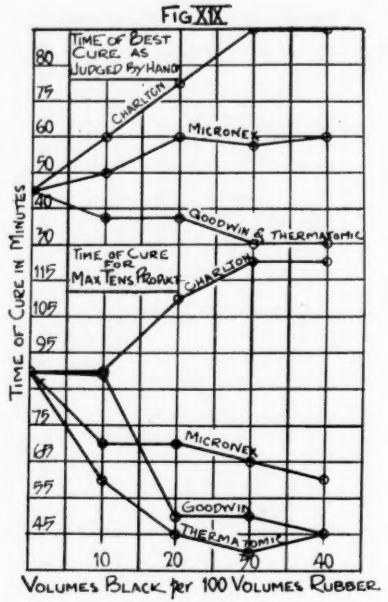


FIG XIX
TIME OF BEST CURE AS JUDGED BY HAND
TIME OF CURE FOR MAX TENS PRODUCT
CHARLTON
MICRONEX
GOODWIN & THERMATOMIC
GOODWIN
THERMATOMIC
TIME OF CURE IN MINUTES
VOLUMES BLACK per 100 VOLUMES RUBBER

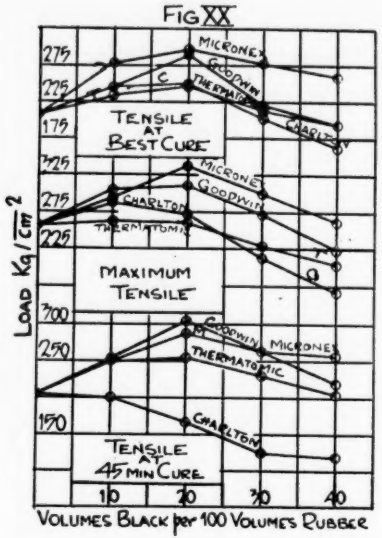


FIG XX
TENSILE AT BEST CURE
MAXIMUM TENSILE
TENSILE AT 45 MIN CURE
MICRONEX
GOODWIN
THERMATOMIC
CHARLTON
LOAD Kg/cm²
VOLUMES BLACK per 100 VOLUMES RUBBER

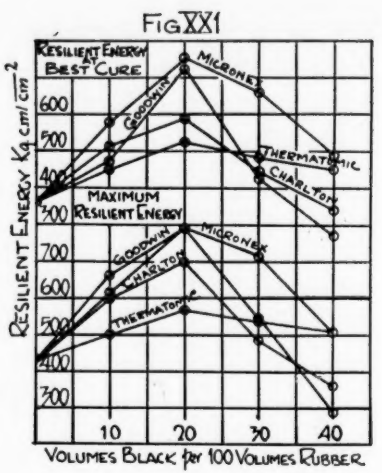


FIG XXI
RESILIENT ENERGY AT BEST CURE
MAXIMUM RESILIENT ENERGY
MICRONEX
GOODWIN
THERMATOMIC
CHARLTON
RESILIENT ENERGY Kg cm/cm²
VOLUMES BLACK per 100 VOLUMES RUBBER

FIG XXII

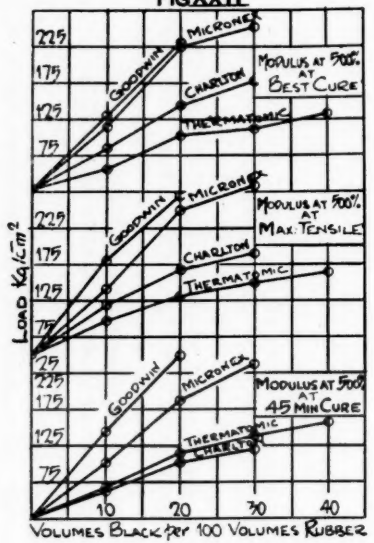


FIG XXIII

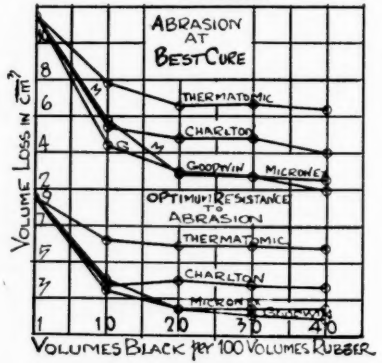


FIG XXIV

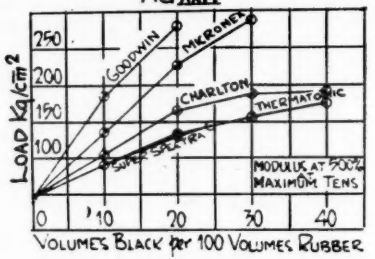


FIG XXV

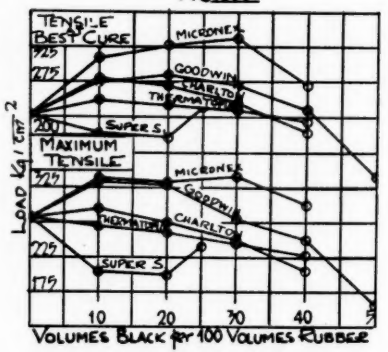
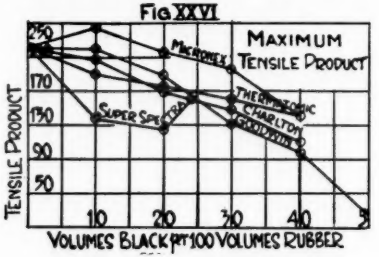


FIG XXVI



physical differences: the particle size, adsorptive capacity, and the general character of the non-carbon adsorbed or included matter.

Table IX—Physical Data—Effect of Acetone-Extractable Matter

Cure at 141° C.	Modulus 300%	Modulus 500%	Tensile	Elongation	Tensile Product
Min.			*Kg./cm.²*		
		ORIGINAL CHARLTON BLACK			
15	23	67	148	700	104
20	30	85	185	700	129
30	40	118	242	700	170
45	47	137	264	690	183
60	52	140	265	685	182
90	62	165	265	650	172
120	67	170	265	660	175
180	62	155	235	620	146
		EXTRACTED BLACK			
15	30	87	195	720	140
20	35	100	222	710	157
30	42	130	265	700	185
45	54	157	290	680	197
60	60	166	292	675	197
90	62	175	305	670	204
120	66	180	305	670	204
180	66	167	240	610	146
		EXTRACTED BLACK WITH OIL[a]			
15	18	60	135	685	93
20	23	70	162	710	115
30	30	95	215	710	153
45	37	115	240	700	168
60	45	135	265	700	186
90	55	150	265	675	179
120	60	150	260	665	173

[a] This sample was not cured in the same mold as the other two.

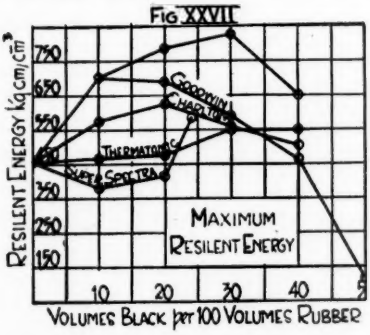
Effect of Particle Size in Rubber—The literature abounds in evidence of the fact that the reënforcing effect of a pigment depends to a large extent upon particle size.[15] The definition of reënforcing effect, however, is rather obscure and several investigators have measured various physical quantities as representing reënforcing effect, such as—hardness, modulus, tensile strength, energy of resilience, and resistance to abrasion. The data presented in this paper show very definitely that these quantities are often in disagreement as to the order in which the pigments arrange themselves. Obviously, therefore, we must have further precise information as to which of the quantities measured indicate the quality for the service intended. It is also evident that if particle size alone were involved the results of the various tests would be identical. There must, therefore, be other very important properties of these pigments which may completely mask the effect of particle size. It is certainly not clear which of the quantities listed above are largely influenced by particle size. It has been pointed out that fineness of division seems closely related to hardness and the reasons have been discussed.

Effect of Particle Shape—The high modulus of stock containing Goodwin black led to the suspicion that the pigment might be rather highly anisotropic. This effect generally shows plainly in the stress-strain curves of strips cut with and across the calender grain, strips cut with the grain

[15] See also Endres, Ind. Eng. Chem., **16**, 1148 (1924).

having a higher modulus. Goodwin black was compared with Micronex in the 30-volume loading. The difference was found to be slightly greater for Micronex than for Goodwin, eliminating this explanation. In general, the differences in the stocks from different blacks have not been of such a nature as to indicate major differences in the shape of the particles. Certain microscopic observations indicate that all the samples are to some extent anisotropic.

Adsorptive Capacity—This is the one property of carbon blacks that exerts the profoundest influence upon the character of a rubber mix. It is probably most strikingly shown by a tendency to retard the rate of cure of the mix. The second effect is the surface-tension effect between the pigment and the medium. If all carbon-black surfaces were identical in nature, it might be possible to choose the optimum grade of carbon black which would give minimum particle size compatible with satisfactory curing. Unfortunately, the problem seems less simple than this, since the adsorption equilibrium between rubber and the curing agents may differ with each type of carbon black. Further studies in adsorption are now in progress.



Choice of a Carbon Black—The choice of a satisfactory carbon black involves so many factors that there is evidently no simple formula. Quite evidently the other ingredients in the mix, especially the accelerator, may determine the order of quality of the blacks. It has been stated previously, and evidence has been presented in profusion, that the physical tests now in vogue do not agree in selecting the black of highest quality. It is apparent that information must be at hand to indicate what test to apply to a stock designed for a certain given service.

One of the most striking facts concerning the tests described is that resistance to abrasion does not parallel either tensile strength or resilient energy. It is apparently a very complicated function of the stress-strain curve in which hardness probably plays a more important role than has hitherto been supposed.

The increased resistance to abrasion with increase in load-

ing seems to be an important addition to our technical knowledge. It appears probable that a certain carbon black apparently inferior to another at equal volume loadings might be so improved by increased loading as to surpass the other.

Effect of Plasticity and Hardness upon Possible Increased Loading—The advantages to be gained from increased loading are limited only by the practical difficulties of handling in the factory and the effect of hardness upon the durability of the tire. Thus, excessive loading of Thermatomic could be accomplished without causing serious trouble in the factory handling of the stock and without making a tread so hard as to cause premature carcass failure in the finished tire. The advantage gained in the way of improved wear, however, would be rather small. Charlton and Goodwin could be increased in loading without meeting serious difficulties in either of the above respects and both would improve in wearing qualities. Increased loading of Micronex would be accompanied by more and more serious trouble in handling while the use of Super Spectra in loadings of over 10 to 15 volumes would be impossible.

FIG. XXVIII

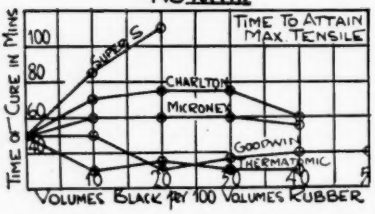


FIG. XXIX

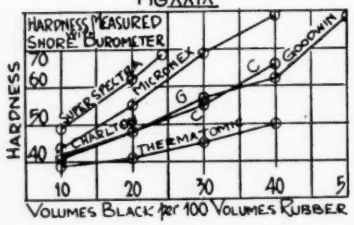
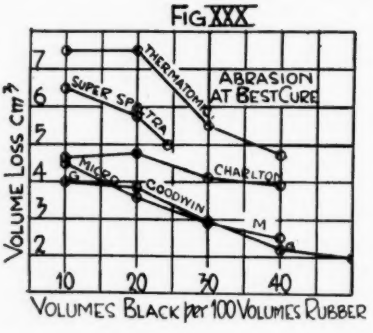


FIG. XXX



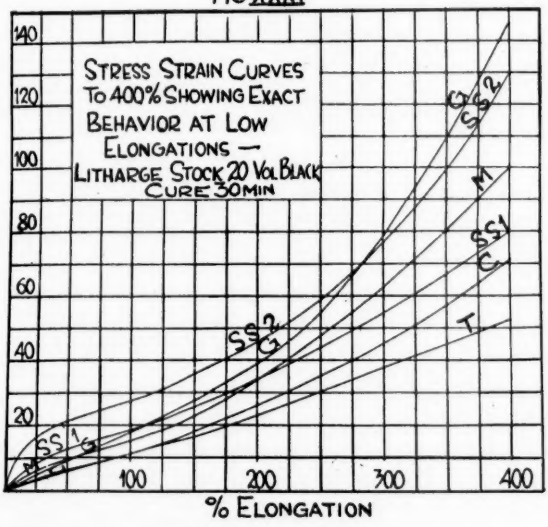
The choice of a carbon black for tire treads should involve the consideration of the resistance to wear at the maximum loading compatible with successful factory manipulation and sound construction.

Effects of Accelerators—It is obvious that Thermatomic and Goodwin black would show to better advantage in stock cured with ethylidene-aniline than in a stock cured with diphenylguanidine. The resistance to abrasion of mercapto stocks is higher than for any other accelerator

tried. This is particularly evident in the behavior of the base stock. A comparison of Table II with the charts of abrasion resistance indicate that this is due largely to the presence of stearic acid in the mercapto stocks, those without stearic acid being about equal to stocks of the other accelerators. Particular emphasis cannot be laid upon this fact in view of the possible lubricating action of stearic acid.

Role of Stearic Acid—The effect of this substance on mercaptobenzothiazole is remarkable. It has been pointed out that the action of stearic acid may stand in some relation to the "livering" of paints in the presence of zinc soaps.

FIG XXXI



The effect is also present in the litharge and in the rubber-sulfur mix, but is less prominent or entirely absent in the other three accelerators tried. It is not presumed that material here presented explains the action of the resin acids but rather that it opens several new avenues of attack upon which further work is in progress.

Acknowledgment

The writers wish to express appreciation for the advice of the research staff of the Goodyear Company, and to Lloyd Cox and Kenneth Eilerts, of this laboratory, whose untiring efforts have been of great value in the preparation of these papers.

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The Mercury Vapor Arc Lamp: Its Uses in a Rubber Factory

P. G. Nagle

Ultra-violet light has recently been brought very prominently into public notice owing to its successful application by the medical profession to the cures of various ailments, and skin diseases in particular; there are, however, many possibilities of its increased application to various industries.

First noticed some 200 years ago, actinic rays were found to produce certain chemical changes in many substances, particularly silver salts; and the artificial production of light containing these rays became a matter of some little importance. Earlier sources for their production were burning magnesium, incandescent calcium oxides, the electric arc between carbon poles, the iron arc, tungsten arc, aluminium and silica arc, etc.

In 1901 a mercury vapor lamp was produced, depending upon the formation of an arc between two columns of mercury in an exhausted glass tube. This lamp, while giving a certain amount of ultra-violet light, lost much of its actinic value owing to the absorption of the greater part of these rays by the glass of the tube, and the main use of the lamp was as a convenient source of monochromatic green light. The substitution of a quartz tube for glass was found to allow a vastly greater amount of ultra-violet light to be transmitted. A great improvement has since been obtained by the production of a lamp giving an arc between mercury columns at ordinary atmospheric pressure. Such a lamp was used in obtaining information which is incorporated in this paper; the actual lamp being a Kelvin Bottomley and Baird "fugitometer," working at 460 volts d. c. The spectrum given by mercury vapor is dependent upon the temperature and nature of the arc, and this must be borne in mind in any attempt at comparative results where different lamps have been used.

In the spectrum of the light emitted by the type of lamp under consideration, the lines are very faint in the red portion of the visible spectrum. A bright orange line at about 5900 tenth-metres being the first distinctly noticeable one; two faint ones about 5000 in the green-blue, and the next of importance in the visible region is a broad one about 4400 in the indigo. Several bright lines occur in the violet about 4100 and a faint one slightly above 4000 at the junction of the visible with the ultra-violet spectrum, which in this latter region extends from 4000 to 2300, and then very faintly to nearly 2100. Incidentally, it is interesting to note that one-quarter inch thickness of plate glass is sufficient to cut off all light having a wave length of less than 3350 tenth-metres. Further reference to this spectrum will be made in the last section of this paper.

There are at least four uses to which such a lamp can be put in the rubber industry; the first three are well known, and will be only briefly considered.

1. As a "fadeometer" or "fugitometer" it is used for the testing of the fastness of dyes to light, either incorporated in rubber or in fabric for proofing. The sample is placed at a definite distance from the quartz tube and exposed for a standard time to the light, the latter falling directly on the sample. Any fading is noted by comparison with an unexposed sample. There are one or two factors affecting fading which have to be considered. (*a*) A certain amount of ozone is formed,

owing to static discharge from the surface of the quartz; this may be removed by a continuous current of air through the apparatus between the tube and the sample. (*b*) The humidity of the atmosphere. To obtain optimum results, the air within the apparatus should be fairly well saturated with water vapor. This condition is usually obtained by having a flat dish of water at the base of the lamp. A fairly standard humidity is obtained, and can be read by a hygrometer attached to the instrument.

2. The lamp is used as an aid to the rapid artificial aging of rubber for test purposes. The sample to be "aged" is treated in much the same way as in the previous experiments. After exposure, physical tests of elasticity and tensile strength are applied and compared with the results obtained from the previous tests on an unexposed sample. A very convenient method is to expose the fold of a piece of rubber bent back upon itself, and to observe the length of time taken for minute cracking on the surface to occur. The results obtained are usually considered in conjunction with the ordinary Geer oven tests.

3. The lamp is used in the examination of lithopones, zinc and titanium oxides and other pigments as to their "sunproof" qualities. Some white substances used as pigments in rubber manufacture, particularly certain qualities of lithopone, are liable to blacken on exposure to sunlight. This peculiarity is well known in the paint trade, which it affects much more seriously than the rubber industry. However, there are several instances of complaints which have arisen regarding white rubber goods which have become slate-grey or nearly black when exposed to the sun. Upon removal from sunlight, the original white color is regained after a lapse of time, partly dependent upon the lithopone used and partly on the time of exposure. It is, therefore, necessary in the manufacture of white rubber shoes, or similar articles, to know if the fillers used are sunproof. For this, the particular lamp under consideration is ideal. The sample of pigment is preferably made into a glycerine paste and exposed in the usual manner. Some samples blacken in a few seconds, others take several minutes. Sometimes the tint is brown rather than black. An exposure of fifteen minutes is usually sufficient to decide whether the pigment is sunproof. The exact reason for the darkening is of no concern at the moment, or the treatment by which a sensitive lithopone can be made sunproof. The darkening in a glycerine paste is almost invariably more rapid than when the same pigment is incorporated in a rubber mixing. In connection with this statement, it is only right to mention that Twiss has had evidence of at least one sample in which the reverse appears to be the case.

4. Finally, the light, after filtration through a Chance ultra-violet screen, may be used in the examination of powders, mixed rubbers and finished articles.

Before going further, it will be as well to consider the nature of the light reaching the sample.

Apart from a certain amount of light with wave-lengths about 7000 tenth-metres, the screen is opaque to all visible light until a wave-length of about 4000 tenth-metres is reached, which is practically the junction of the visible violet with the ultra-violet. The screen rapidly becomes transparent to shorter wave-lengths until at about 3700 tenth-metres 50 per cent of the light is transmitted. To shorter wave-lengths the screen is less transparent until it becomes opaque to waves shorter than 3050 tenth-metres. The main portion of the transmitted light which reaches the sample will, therefore, be that of wave-lengths between 3300 and 3900, and particularly 3600 to 3700 tenth-metres.

As most of these waves are outside the power of human vision, a normally white surface would be expected to appear violet when viewed by reflected light obtained under these conditions, since this is the only visible light emitted by the screen.

In some cases this is so, but the reflected light from the surfaces of many apparently white powders gives rather unexpected results. It would take up too much time to consider more than one or two cases, and the discussion will be restricted to a few zinc oxides and lithopones. Eight samples of zinc oxides in the form of glycerine pastes were painted on a black surface. In ordinary daylight they were indistinguishable, all being of a good white color. Three samples, labelled *A*, *B* and *C*, were of different grades from the same producer, two, *D* and *E*, different grades from another manufacturer, *F*, *G* and *H* from separate sources, while *I* was analytically pure zinc oxide. When viewed in a beam of the filtered light all eight samples gave different colors or shades of color. *A*, *B* and *C* all appeared light green, *B* slightly greyer than *A*, and *C* greyer again than *B*. *E* and *F* were distinctly orange-buff, *F* being duller in tone than *E*. *G* gave a fine bright apple-green color. *H* gave an impression of dull violet, rather pale in tone, while *I*, the pure sample, gave a rich deep violet, very similar to the color observed on looking directly through the screen.

Subsequent samples of different deliveries from the previous sources of origin gave identical results with those previously observed. The experiment being reversed, i. e., samples examined without knowledge of their identity, it was a very easy matter to pick out the various qualities, grades and sources of supply.

A rubber mixing was made up having the following composition: Pale crepe, 200 parts; lithopone, 50; sulfur, 4; vulcafor VI, 2. This was divided into three parts, and 2 per cent of zinc oxide *A* sample, 2 per cent of *E*, and 2 per cent of *I* milled into the three small batches.

Since lithopones themselves, as will be remarked upon later, give different colors in the filtered light, the lithopone chosen was one which gave a deep violet. These samples being viewed before and after cure in the ultra-violet filtered light, showed, in both cases, exactly the types of color previously given by the zinc oxide pastes. Equal amounts of carbon black were next introduced into the three samples until a dark slate color was produced. Upon viewing these samples under the screen, it was perfectly easy to separate them and to tell which zinc oxide was present—the actual apparent color being, of course, different from those given by the white mixes, but only in the greyness of the orange, green and violet.

Exactly the same phenomenon occurs in the lithopones, but in the samples examined the variation in apparent color was not so distinct. Sixteen samples gave four distinct types: those giving (1) a deep violet; (2) a pale violet color; (3) a brown color; and (4) those appearing almost pure white.

It is interesting to observe that those lithopones giving a deep violet were sunproof or practically so. those giving a brown color were affected to some extent, while the white type were known to be very susceptible and to darken in a few seconds in the direct light of the arc. Samples of the latter type, however, after fifteen minutes' exposure to the filtered light, showed no darkening. It would appear, therefore, that the rays causing the phenomenon of darkening are of shorter wave-length than those transmitted by the screen; that is, less than 3000 tenth-metres.

Mineral oils, vaseline, etc., exhibit a fluorescence or phosphorescence, appearing self-luminous.

Coal tar itself exhibits a faint yellow-brown fluorescence, but when incorporated in a black rubber mixing gives the whole a light grey-blue tone. Two black mixings of the same composition, except that one contained 1 per cent of coal tar, appearing much the same in ordinary light (the coal-tar mix being slightly blacker) appeared very dark violet and grey-blue when viewed in the filtered light.

Sulfur appears as a bronze powder, as far as we have ascertained from various samples.

Very many other substances of both organic and inorganic nature give characteristic appearances.

The value of being able to ascertain at a glance whether an article containing several different mixings of similar appearance and color is correctly made up needs no emphasis. That such a thing is at least possible can easily be demonstrated by examination of such an article in the filtered light.

An even-colored dull black boot was made, having the leg, vamp, heel and sole portions of different composition; each part showed a distinctly different color under the screen.

Sections of tires are extremely interesting, showing all variations of apparent color: violet, brown-violet, blues, greens, yellows and brown-reds.

Already much saving of time and labor has been made in being able to see in a few seconds whether a doubtful mix is correct or whether it is *A*, *B* or *C* quality. It might even be worth while to make slight changes in existing mixes of the same apparent color by the addition of very small quantities of a substance, producing a change of appearance in the mix when observed in the light from the combined screen and lamp, provided always this addition would not change the physical or aging properties of the rubber.

It is by no means suggested that different mixings all show different colors; the reverse is more probably the case. Neither can the composition of a mix be more than suggested even in the most favorable circumstances, but it must be remembered that only the fringe of the subject has yet been explored.

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Latex Contaminated with Copper Compounds as a Source of Danger of Fire

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A textile factory in Holland made double texture cotton fabric by applying a layer of latex to one of the fabrics and passing both fabrics through a calender, after which they were dried and pressed together. From the calender the double texture was rolled up immediately without previous cooling and the big rolls were stored.

Shortly after storage a smell of burning was noticed in the store-room, and on closer inspection it appeared to emanate from the rolls. On opening these rolls it was found that the color of the fabric had turned from white to light brown. The cloth had lost its suppleness and could be readily torn. In the interior of the roll the cloth was scorched and even locally charred. One got the impression that the rubber in the cloth was severely oxidized, i. e., resinified. The problem to be solved was what caused this strong oxidation, which eventually led to spontaneous combustion.

According to information received from the mill, the latex was placed in a brass tank and it also came in touch with a brass roller. From further information it became evident that the ammonia, which is added to the latex as a preservative, dissolved copper out of the parts of the machine mentioned. In this way the cloth was covered with a layer of rubber in which copper compounds were evenly distributed. As copper and copper compounds have an extraordinary accelerating effect on the oxidation of rubber and oxidize the latter in a very short time even at ordinary temperature, it was clear that the oxidation mentioned above was caused by the contamination of the latex with copper compounds.

On investigating[1] the samples supplied by the factory, it was found that the original cloth did not contain any copper. However, the ash of the fabrics treated with latex showed a very distinct copper reaction, which explains the oxidation of the rubber.

That this oxidation under certain conditions can proceed so quickly, and with so great a development of heat, that spontaneous combustion occurs, was not known to us and therefore it seemed desirable to prove the tendency for spontaneous combustion of latex-treated fabrics in the presence of copper.

For this purpose an apparatus was used, which has been designed by Mackay,[2] to test the tendency for spontaneous combustion of oil-proofed cloth. This apparatus proved to be very useful for our purposes.

The apparatus is shown in Figure 1. In a water-bath, A, an air-bath, B, is suspended. The pipes C and D permit of circulation of air. The material to be tested, F, is placed in a gauze cylinder, E, around a thermometer. When the water in A is boiling, the temperature in B is about 92° C.

[1] For carrying out these experiments we are indebted to the Netherlands Rubber Institute at Delft for the hospitality offered to us.

[2] See Dr. J. Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," III, 99 (1915).

If the material under test has a tendency for spontaneous combustion, the thermometer rises considerably above 92° C.; if this tendency is absent, the thermometer keeps indicating the temperature of the air-bath.

From the cotton supplied by the manufacturer three samples were prepared:

I. Cloth impregnated with pure ammoniated latex;

II. Cloth impregnated with a copper oxide-ammonia solution;

III. Cloth impregnated with latex containing copper oxide-ammonia, prepared by suspending a copper spiral in the latex during 24 hours.

This latex contained 290 mg. copper per liter, an amount insufficient to produce a blue color of the latex. The amount of copper in the latex-treated fabric was approximately 40 mg. per square meter.

The cloth was wrapped tightly around the thermometer, the roll having a diameter of 3.5 to 4 cm.

The dotted line of Figure 2 represents the temperature of the air-bath. From

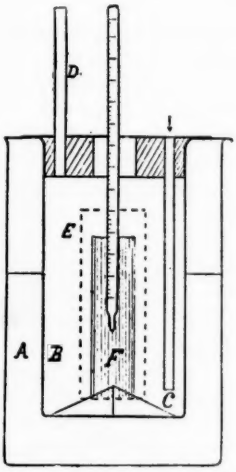

Figure 1—Mackay's Apparatus

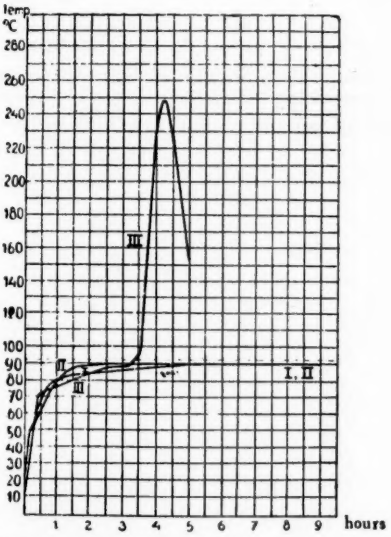

Figure 2—Change of Temperature in Various Samples when Heating to 92° C.

the curves I and II it appears that cotton cloth impregnated with pure ammoniated latex or with a solution of copper oxide-ammonia take the temperature of the air-bath, and therefore do not show the slightest tendency for spontaneous combustion or even a rise in temperature caused by oxidation. After about 8 hours' heating, the samples did not show any alteration.

On the other hand the temperature in the fabric treated with latex containing copper rose very quickly after the temperature of the air-bath had been reached. In about 45 minutes the thermometer indicated 249° C. Apparently the rubber was then completely oxidized, as the temperature came down quickly. When opening the roll the fabric around the mercury reservoir of the thermometer appeared to be scorched. About 2 cm. above the reservoir probably a still higher temperature had been attained, as on that place the cloth was partly charred and even locally burnt to a white ash. On the inside of the air-bath and of the outlet, there was a deposit of tarry distillation products of the rubber.

These results not only confirm the fact, well known to every rubber chemist, that copper compounds oxidize and resinify rubber very quickly, but also that under certain circumstances this oxidation proceeds so rapidly, and therefore with so great a development of heat, that spontaneous combustion and serious danger of fire result.

In the case in question the spontaneous combustion had been accelerated:

(1) By tightly wrapping the cloth when still warm, which caused the oxidation to start at once with a noticeable velocity.

(2) By the rather large diameter of the roll of cloth, which conducted the heat badly, so that the heat developed in the interior could only escape very slowly. This results in a rise in temperature which greatly accelerates oxidation, and the initial temperature necessary for spontaneous combustion is soon attained.

The oxidation of latex-treated cloth and the danger of spontaneous combustion can be prevented by taking care that the ammoniated latex does not come into touch with copper or brass alloys. All parts of machinery and utensils made from these metals should be replaced by parts made from other materials which are not affected by ammonia or have not an oxidizing influence on rubber, for instance, aluminium, wood, rubber, etc.

If this precaution is carefully observed, latex can be of excellent service for the purpose described and no danger of fire is to be feared.

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Plasticity Determinations in Crude Rubber. Influence of Different Factors on the Changes in Plasticity When Keeping the Rubber

O. de Vries

RUBBERPROEFSTATION IN NEDERLANDSCH-INDIË

In preceding communications[1] we discussed the influence of different factors in the composition of the latex and in the preparation of the rubber on the plasticity of the crude product. It was found that this influence is in general rather small; the difference in plasticity, found in the samples from some estates and in rubber prepared according to special methods, could not be explained in this way, and our results did not clear up the complaints from manufacturers on variability in plasticity in the estate product.

The explanation that offered itself in the first place was that the crude product changes in plasticity on keeping, and that different factors affect these changes in one sense or the other. Changes on "freezing" in the warehouses in Europe are outside our field of work; it was, however, soon evident that keeping in the tropics, that is, at an even temperature of 25–30° C., causes some samples to get harder and others to get softer. We already pointed out on a former occasion[2] that different special types (Kerbosch rubber, l. s. rubber, hard fine, etc.) get very hard on keeping; from the figures obtained in our first experiments it seemed that ordinary crepe also gets harder on keeping, and, although originally a somewhat more plastic type than smoked sheet, is on the average harder than the latter after a year or so. In other cases the D_{30} decreased more or less slowly without there being question of stickiness and still less of tackiness or decay.

To obtain a general impression of the factors that play a role in the changes in plasticity on keeping, we have tested again, after keeping them for one or two years, a number of samples described in former communications. In this communication we give a review of the results and hope to publish at a later occasion the figures obtained in special experiments, planned to investigate the points that stood out as important in this preliminary review. The results may be summarized as follows:

1. *Young or backward trees.*

Some of the samples got softer, others harder; a regular influence of this factor is not found. On the average the samples became slightly harder (average + 0.04 in D_{30}); a striking softening of the already originally somewhat weak rubber from young trees was not found.

2. *Sodium acetate.*

A sample from latex to which sodium acetate had been added showed a decrease

[1] *Archief*, **IX**, 260, 435, 459 and 837 (1925).
[2] *Ibid.*, **IX**, 459 (1925).

in D_{30} from 1.41 to 0.83 in two years, so that it had become rather weak; the control showed no change. This point deserves further investigation.

3. Amount of acetic acid.

The figures for some series of samples, coagulated with different amounts of acetic acid, have been published already.[3] Repeat tests after 1, 2 and 3 years, respectively, gave no distinct influence of a dose of 1:40, as compared with 1:80 and 1:160. The same was the result with the other series,[4,5] in which the plasticity of the fresh samples had not been determined and the first test was made about $^1/_2$ year after preparation. Repeat tests 1 and 2 years after preparation gave no indication that the amount of acid, used for coagulation, has an influence on the changes in plasticity on keeping.

4. Amount of formic acid.

The changes in plasticity were also determined for different amounts of formic acid; from the figures published in the above-quoted communication it is evident that the amount of formic acid has no influence, and also that formic acid gives the same results as acetic. Some further series corroborate this.

5. Alum and sulfuric acid.

A sample prepared with alum showed only a small change in two years (increase in D_{30} of 0.06).

A sample prepared with a very large dose of sulfuric acid, that originally showed a D_{30} of only 1.05, had got harder after two years and showed a D_{30} of 1.27. Deterioration, even with this very large dose of sulfuric acid, had not taken place.

6. Dilution of the latex.

Taking separately from one of the series of sheet and crepe samples, two sets of samples from undiluted latex, one set from latex diluted 1:1 and two sets from latex diluted 1:9, we get:

	Latex					
	Undiluted		1:1		1:9	
	D_{30}	Slope	D_{30}	Slope	D_{30}	Slope
Fresh	1.45	0.06[5]	1.54	0.07	1.45[5]	0.09
After one year	1.38[5]	0.08	1.38	0.08	1.21	0.10[5]
Difference	−0.06[5]		−0.16		−0.24[5]	

It will be seen that the more diluted the latex, the more D_{30} decreases on keeping.

Three sets of samples from another series gave:

	Latex			
	Undiluted		1:1	
	D_{30}	Slope	D_{30}	Slope
Fresh	1.51	0.07	1.51	0.08
After one year	1.67	0.07	1.58[5]	0.07
Difference	+0.16		+0.07[5]	

In this case also there was a difference in the same direction.

Further examples of the influence of the dilution of the latex will be given in a following communication.

7. Effect of milling.

The sample that had been softened by prolonged milling (ten minutes on our small laboratory mill) and showed a D_{30} of 0.83, showed a further decrease to a D_{30} of 0.73 in the course of two years. A decided softening had not taken place.

[3] *Archief*, **XI**, 355 (1927).
[4] *Ibid.*, **XI**, 358 (1927).
[5] *Ibid.*, **XI**, 360 (1927).

Of the samples from an experiment on an estate, sheet got harder on keeping, from 1.52 in 13 months to 1.74 and in 19 months to 1.80. Crepe prepared in the ordinary way (five times through the macerator) had originally a somewhat smaller D_{30} than the sheet, viz., 1.46; on keeping it increased to 1.58. The crepe got somewhat harder on keeping, but not so hard as the sheet. A sample that had been treated longer in the first mill did not get so hard or even got somewhat softer; the differences in D_{30} were:

	After 13 months	After 19 months
Sheet	+0.22	+0.28
Crepe, milled 5 times in masticator	+0.12	+0.12
Crepe, milled 10 times in masticator	+0.05	+0.08
Crepe, milled 20 times in masticator	−0.05	−0.02
Crepe, milled 40 times in masticator	0	−0.03

These differences, of course, may have been influenced by the mechanical treatment but also by the removal of serum substances by washing.

In another experiment on an estate, in which an extra 10 times' milling was given in the different mills, not much difference could be found after one year; the control had decreased from 1.50 to 1.32, the extra milled samples decreased only from 0.04 to 0.11 in D_{30}.

It is evident that extra milling causes only small differences in plasticity on keeping the crepe; perhaps these differences are only to be ascribed to a removal of serum substances by washing and not to the mechanical treatment.

8. Sheet and crepe.

Nine series of samples, in which unsmoked sheet, dried without heat, were compared with crepe, gave the following figures:

	Sheet		Crepe	
	D_{30}	Slope	D_{30}	Slope
Fresh	1.62	0.08[5]	1.38	0.07
After one year	1.80[5]	0.08	1.45	0.06[5]
Difference	+0.18[5]		+0.07	

Both types got harder on keeping, but the sheet more so than the crepe.

A further series of five sets of sheet and crepe, each set being prepared from one lot of bulked latex, gave:

	Sheet		Crepe	
	D_{30}	Slope	D_{30}	Slope
Fresh	1.52	0.08	1.42	0.07
After one year	1.38	0.09	1.24	0.09
Difference	−0.14		−0.18	

In this case all the samples got softer, but the crepes more so than the sheet. The cause of the decrease in D_{30} was found in the dilution of the latex (compare §6 above).

That crepe increases less in hardness than unsmoked sheet, or increases more in plasticity, can again be ascribed to a lower content of serum substances and need not be ascribed to the mechanical treatment.

We further compared samples from latex 1:9; the coagulum contains only a relatively small amount of serum substances (ash content of the rubber about 0.08%) and more or less washing makes only little difference. Part of the coagulum was cut to small pieces and dried without washing or mechanical treatment; another part was rolled to sheet (small amount of washing and rolling) and air-dried, the rest was creped. This gave:

	Ash	Fresh D_{30}	Fresh Slope	After 1 year D_{30}	After 1 year Slope	Difference in D_{30}
Cut with scissors	0.09	1.51[5]	0.09[5]	1.35	0.10	−0.16[5]
Sheet	0.07	1.53	0.09[5]	1.33	0.09[5]	−0.20
Crepe	0.10	1.38	0.09	1.09	0.11	−0.29

There was a distinct difference.

9. Washing with water during milling.

The influence of the different factors that play a role in milling to sheet or crepe were investigated separately. Milling with and without water means pressing out some serum in the one process, and removing the serum as completely as possible in the other process. The average of four sets of samples gave:

	Ash	Fresh D_{30}	Fresh Slope	After 1 year D_{30}	After 1 year Slope	Difference in D_{30}
Sheet, without water	0.46	1.51	0.07[5]	1.56	0.08	+0.05[5]
Sheet, with water	0.38	1.54	0.08	1.50	0.08	−0.04
Crepe, without water	0.28	1.40	0.06[5]	1.37	0.07	−0.04
Crepe, with water	0.27	1.44	0.06[5]	1.37	0.07	−0.07

The rubber washed with water has therefore increased more in plasticity than the unwashed rubber, and the difference is larger for sheet than for crepe, in which latter the mechanical treatment without washing already removes more serum.

Similar experiments were taken with coagulum from latex 1: 9, which contains less serum substances. The average from two series was:

	Ash	Fresh D_{30}	Fresh Slope	After 1 year D_{30}	After 1 year Slope	Difference in D_{30}
I. Cut	0.09	1.51[5]	0.09[5]	1.34[5]	0.10	−0.17
Sheet, without water	0.10	1.58[5]	0.09[5]	1.34[5]	0.10	−0.24
Sheet, with water	0.07	1.53	0.09[5]	1.32[5]	0.09[5]	−0.20[5]
II. Crêpe, without water	0.09[5]	1.37	0.09[5]	1.10	0.11[5]	−0.27
Crêpe, with water	0.10	1.38	0.09	1.09	0.11	−0.29

The differences are only small and for the sheet not in the same sense as above.

10. Extraction of unmilled coagulum.

The average of four series was:

Description	Ash content, %	After 1 month D_{30}	After 1 month Slope	After 1 year D_{30}	After 1 year Slope
Coagulum not soaked, afterwards sheet	0.19[5]	1.61	0.08	1.39	0.09
Coagulum soaked in water, afterwards sheet	0.11	1.54	0.09	1.24	0.10
Coagulum not soaked, afterwards crepe	0.15	1.52	0.07	1.37	0.08
Coagulum soaked, afterwards crepe	0.13[5]	1.48	0.07[5]	1.29	0.09

Soaking during one night has therefore caused the rubber to get somewhat more plastic on keeping, but the difference is not large; the extraction has naturally only a small effect on a block of coagulum that in ratio to its weight has only a small surface.

11. Extraction of freshly milled rubber.

Soaking freshly milled sheet in water has more effect: the sheets are so thin that the water can extract a large portion of the soluble substances. Two series gave on the average:

	Ash	After 1 month D_{30}	After 1 month Slope	After 1 year D_{30}	After 1 year Slope	Difference in D_{30}
Unsmoked sheet, not soaked	0.28	1.51	0.06[5]	1.53	0.09	+0.02
Unsmoked sheet, in water one night	0.10	1.39	0.13	1.06	0.11	—0.33

The difference is marked, the extracted sheet got much weaker on keeping and the non-extracted sheet got somewhat harder.

The effect was less striking in three series, prepared on an estate, although the extraction had been efficient, as may be seen from the figures for ash and time of cure. The figures were:

	Ash	Time of cure	After 1 month D_{30}	After 1 month Slope	After 1 year D_{30}	After 1 year Slope	Difference in D_{30}
Smoked sheet, not soaked	0.26	120	1.50	0.06^5	1.51	0.07	+0.01
Smoked sheet, one night in water	0.11	110	1.46	0.07	1.42	0.07	—0.04

The effect is small but in the same sense as above.

12. Heating.

Slight heating, as used in the drying of sheet rubber, has little influence on the changes in plasticity on keeping. A series of nine sets of samples, dried in the air without heating or during the day at 35° (without smoking), gave the following figures:

	Fresh D_{30}	Fresh Slope	After 1 year D_{30}	After 1 year Slope	Difference in D_{30}
Not heated	1.63^5	0.08^5	1.81	0.07^5	$+0.17^5$
Dried at 35°	1.66	0.09	1.76	0.08^5	+0.10

In two experiments, in which unsmoked sheet and crepe were dried in the air, at 40, 50 and 70°, no difference was found in the changes in plasticity on keeping; all the samples showed about the same decrease in D_{30} on keeping. In a third experiment, in which films from evaporated latex were treated in the same way, the temperature of drying also had no appreciable influence; the films all got harder on keeping, in the average as follows:

	D_{30}	Slope
Fresh	1.52	0.06^5
After 2 months	1.64	0.07
After 4 months	1.68^5	0.06^5
After 6 months	1.68	0.07

This hardening of rubber that contains all the serum substances and that we have described already for different "special types" will be discussed further in a following communication.

When fresh crepe is dried at higher temperature, be it in the air (in a drying stove) or in vacuo, the plasticity increases somewhat more on keeping.

	Fresh D_{30}	Fresh Slope	After months	D_{30}	Slope	Difference in D_{30}
Dried at ordinary temperature	1.60	0.08	13	1.56	0.07	−0.04
Dried at 90°	1.64	0.08	13	1.50	0.07	−0.14
Dried at ordinary temperature	1.46	0.06	27	1.39	0.06	−0.07
Dried at 80° in vacuo	1.45	0.08	27	1.30	0.07	−0.15

In an experiment in which the freshly milled crepe was kept during two hours in water of 90° the effect was not large. D_{30} decreased from 1.44 to 1.33, a decrease of 0.11 against 0.07 for the control. One would have expected a larger difference on account of the extraction with water, and this result will have to be controlled by further experiments.

13. Heating and smoking.

An experiment in which three sets of sheet were dried in the air at ordinary temperature and in a smokehouse, respectively, gave on the average the following results:

	Not smoked		Smoked	
	D_{30}	Slope	D_{30}	Slope
Fresh	1.61[5]	0.08[5]	1.49[5]	0.07[5]
After 2 months	1.53	0.07[5]	1.56	0.07[5]
After 3 months	1.67	0.08	1.64	0.07[5]
After 4 months	1.74	0.08	1.61	0.09
After 12 months	1.58	0.08	1.56	0.09

The figures are not quite regular, but a distinct difference caused by the heating is not found.

Two sets of samples of crepe, treated in the same way, gave:

	I				II			
	Dried in the air		Smoked		Dried in the air		Smoked	
	D_{30}	Slope	D_{30}	Slope	D_{30}	Slope	D_{30}	Slope
Fresh	1.35	0.07	1.35	0.07	1.44	0.06	1.27	0.06[5]
After 1/2 month	1.38	0.06	1.34	0.08	..	..	..	..
After 1 1/2 months	1.35	0.06[5]	1.38	0.06[5]	..	..	..	..
After 2 months	1.33	0.06[5]	1.54	0.10	..	..	..	..
After 3 months	1.33	0.06	1.49	0.09	..	..	..	..
After 6 months	1.34	0.06[5]	1.52	0.08	..	..	..	..
After 12 months	1.21	0.08	1.29	0.07	1.46	0.07	1.16	0.07[5]

The smoked crepe therefore got harder on keeping, and afterwards soft; the air-dried crepe remained constant in plasticity at first and got softer later on. These changes will have to be studied more in detail.

Four sets of sheet, dried in different ways, gave on the average:

	Fresh		After 1 year		Difference in D_{30}
	D_{30}	Slope	D_{30}	Slope	
Ordinary temperature	1.49	0.07	1.50[5]	0.07[5]	+0.01[5]
Heated (without smoke)	1.56	0.06[5]	1.65	0.08	+0.09
Smoked (with heat)	1.51	0.06[5]	1.53	0.08[5]	+0.02

Heating the rubber has made it harder in this case, in contradiction with the (small) difference in the opposite sense found on a former occasion (see above).

Speaking generally it is clear that the influence of heating and smoking is not pronounced; some details will have to be investigated further.

14. Coagulation by alcohol.

In four series of samples the following figures were obtained:

	Fresh		After 1 1/2–2 years		Difference in D_{30}
	D_{30}	Slope	D_{30}	Slope	
Control	1.50[5]	0.06[5]	1.41[5]	0.06[5]	−0.09
Alcohol	1.46	0.06	1.31	0.07	−0.15

Rubber coagulated by alcohol seems to get somewhat softer on keeping than the ordinary acetic acid product; but the difference is not large.

15. Coagulation by heat.

In two experiments the samples from latex coagulated by heating showed about the same change in plasticity as the acetic acid controls (decrease in D_{30} 0.09 on the average, as compared with 0.06 for the control).

16. Maturation.

For crepe from matured rubber a series of figures was already given on a former occasion;[6] the average was:

	D_{30}	Slope
Fresh	1.61[5]	0.09
One year old	1.77	0.07[5]

[6] *Archief*, **IX**, 463 (1925).

so that the crepe got somewhat harder on keeping.

Remarkable changes were observed in some samples from matured coagulum. The control (not matured) had got somewhat harder after keeping one year (D_{30} increased from an average of 1.37 to 1.48); the crepe from matured coagulum showed a larger increase (from 1.43 to 1.69), but coagulum cut to fine pieces and kept without washing or creping had become very soft (decrease in D_{30} from 1.60 to 0.94). In a former communication[7] we described that matured coagulum, when kept in the air, gets weak and tacky on the outside, where it is in contact with the air; it is not astonishing that finely cut coagulum behaves in the same way. Crepe from matured coagulum shows, as is well known, considerable changes on keeping (decrease in viscosity, increase in time of cure); in the above experiments the crepe from matured coagulum hardened somewhat more on keeping than ordinary crepe, while the coagulum dried without washing got very weak. By the washing and creping of the coagulum certain substances have therefore been removed that have a large influence on the changes in plasticity.

17. Rubber from ammoniated latex.

In a former communication[8] we mentioned figures for rubber from ammoniated latex. In two series from ammoniated latex of different age the plasticity was on the average:

	D_{30}	Slope
I. Fresh	1.59	0.13
After 1 year	1.47	0.09[5]
II. Fresh	1.55	0.08[5]
After 1 year	1.43[5]	0.07[5]
After 2 years	1.21	0.10

The rubber therefore got more plastic on keeping.

Another series gave, in comparison with the control sample from fresh latex:

	Control		Rubber from ammoniated latex	
	D_{30}	Slope	D_{30}	Slope
Fresh	1.59	0.08	1.52[5]	0.08
After 1 year	1.49	0.06[5]	1.42[5]	0.07
After 2 years	1.37	0.06[5]	1.33[5]	0.07[5]

The rubber from ammoniated latex therefore increased about as much in plasticity as the control.

Films from ammoniated latex, evaporated on the air, had already got very hard after 6 months (D_{30} 1.89 and 2.09); in a later communication we will give further examples of such changes. This is the same phenomenon as we already described above, viz., that the presence of all the serum substances causes the rubber to get harder.

Summary

Rubber that contains less than the normal proportion of serum substances shows a larger increase in plasticity on keeping than the ordinary plantation product. Coagulation from latex diluted 1:1 has a distinct effect, coagulation from latex diluted 1:9 has a marked effect in this direction; extraction by soaking in water, or washing during milling, may have an appreciable effect.

As rubber that contains all the serum substances gets harder on keeping, there must be—presumably at a content of serum substances in the region of that of normal plantation rubber—a point where the plasticity remains about constant

[7] *Archief*, **XI**, 71 (1927).

[8] *Ibid.*, **XI**, 343 (1927), see especially Table XXXVII on page 339, Table XXXV on page 337 and Table XXXVIII on page 340.

on keeping. This proportion of serum substances may be regarded as the most desirable from the standpoint of uniformity, especially constancy in plasticity on keeping.

The changes in plasticity on keeping are little influenced by the age of the trees (soft rubber from young trees changes little on keeping), by the nature of the acid (acetic or formic) and the proportion of acid used for coagulation, by mechanical treatment (rolling to sheet or crepe, milling a smaller or larger number of times), by heating during drying and by smoking.

The rubber gets very weak on keeping when a large dose of sodium acetate had been added to the latex; finely cut (not washed) pieces from matured coagulum get very weak on keeping, in contrast to crepe from matured coagulum that gets somewhat harder on keeping, about as or somewhat more so than ordinary crepe.

Coagulation by heating has little influence; coagulation by alcohol seems to cause the rubber to get somewhat softer on keeping. Crepe from ammoniated latex changes about in the same way as the control from fresh latex; films from ammoniated latex evaporated in the air got very hard on keeping, just as films from fresh evaporated latex.

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The Effect of Heat on Raw Rubber in the Presence and Absence of Air

J. D. Fry and B. D. Porritt

During the process of milling or masticating rubber, three agents, namely, mechanical working, heat, and the constituents of the air, are evidently present which may be individually or collectively responsible for the resulting physical changes. The generally accepted explanation of the effects produced is that the mechanical treatment breaks down some form of structure existing in the raw rubber or rubber particles and consequently it is customary to describe material as "overworked" when milling has been carried too far, and to reserve the terms "burnt" and "scorched" for cases in which the heat generated in the process has caused premature vulcanization.

The correctness of the assumption that milling is essentially a mechanical operation at first sight seemed to be supported by an experiment made by one of the authors in which the treatment was carried out under a stream of cold water when it was found that the solution viscosity of the material diminished in much the same way as in the normal process, the only apparent difference in the final product being the almost complete absence of the adhesiveness characteristic of milled rubber. Further consideration, however, suggested that though the conditions under which the test was made undoubtedly minimized contact with air and the development of heat, the possibility that oxygen might still play a part was not entirely excluded, while the fact that the bulk of the rubber was kept cold did not necessarily preclude local rises in temperature taking place in the material when passing between the rolls.

It therefore seemed clear that more evidence was required before the results of the rough works experiment could be accepted as conclusive and the effects of heat and air in the milling process assumed to be limited merely to causing the development of tackiness. With this object, a preliminary test was made to determine the effect produced on the solution viscosity by heating rubber in air for definite times to temperatures varying from 100° C. to 150° C., which were judged to be values approximating those which the material was likely to experience in the normal process of milling.

For this purpose a sample of plantation crepe was employed, small quantities being weighed into test tubes, which were then inserted in a glycerin bath maintained at the desired temperatures. Subsequent examination of solutions of the treated samples in comparison with one prepared from the original material showed that the solution viscosity was lowered by the heat treatment, and that the lowering was most marked in those samples which had been subjected to the higher temperatures. The result confirmed the suspicion that heat played an important part in the changes taking place in the process of milling and recalled the practice adopted in the early days by Thomas Hancock, who prepared his rubber for factory use by heating it in a baker's oven ("Origin and Progress of India Rubber Manufacture," p. 15), and it was decided to investigate the matter more thoroughly throughout a definite range of temperatures, and to compare the effect of heat alone with that produced by milling under ordinary technical conditions.

By the courtesy of one of its members, the Research Association was supplied with a series of samples removed from a batch of plantation rubber at different stages in the milling process, together with a specimen of the original material. The latter was cut into fine shreds and portions of 3 g. each were weighed out into a series of thin-walled test tubes for subjection to heat treatment, this being carried out by immersion in the vapors of the following series of constant boiling liquids giving a range of temperatures from 106° C. to 178° C.

Acetic acid (dilute)	106° C.
Acetic acid (glacial)	115° C.
Xylene	137° C.
Anisole	150° C.
Aniline	180° C.

The tubes were left open to permit free access of air, and four tests made at each temperature to determine the effect of varying the time of heating from a period of 30 minutes up to one of 4 hours. After treatment the tubes were allowed to cool and the contents added to 97 cc. of benzene in stoppered bottles, which, after the lapse of sufficient time to allow the rubber to swell, were thoroughly shaken for an hour in a mechanical shaker.

The viscosities of the resultant solutions were compared by means of an instrument of the Ostwald type, precautions being taken throughout to exclude any effect due to light. The concentration of the rubber was then reduced to 2 per cent strength by the addition of more benzene and the viscosities redetermined in order that the relation between the values might be more clearly indicated in the case of those samples giving high values.

The results are shown in Table I, the viscosities being expressed as the number of seconds taken by the various solutions to pass between two marks on a standard viscometer.

TABLE I

Temperature, ° C.	Time of heating, hours	Relative viscosity	
		2 per cent solution	3 per cent solution
106	0.5	Very large	Very large
106	1.0	2691 sec.	Very large
106	2.0	2031	Very large
106	4.0	1434	Very large
115	0.5	1797	Very large
115	1.0	1478	Very large
115	2.0	1213	Very large
115	4.0	863	Very large
137	0.5	532	2508 sec.
137	1.0	296	1165
137	2.0	134	411
137	4.0	86	230
150	0.5	141	500
150	1.0	77	203
150	2.0	33	68
150	4.0	24	47
180	0.5	77	204
180	1.0	45	101
180	2.0	42	91
180	4.0	30	62

Solutions of 2 per cent and 3 per cent strengths were also prepared from the corresponding range of milled samples, and the viscosities determined under similar conditions and with the same instrument.

The values obtained are shown in Table II.

TABLE II

Time of milling, minutes	Relative viscosity 2 per cent solution	3 per cent solution
10	344	1594
20	231	908
30	170	613
40	151	437
50	130	388
60	109	323
75	94	274
90	86	234
105	77	210
120	71	193

The results of these experiments are illustrated graphically in Figures 1, 2, 3 and 4. The curve in No. 4, representing the effect of milling, takes the usual form

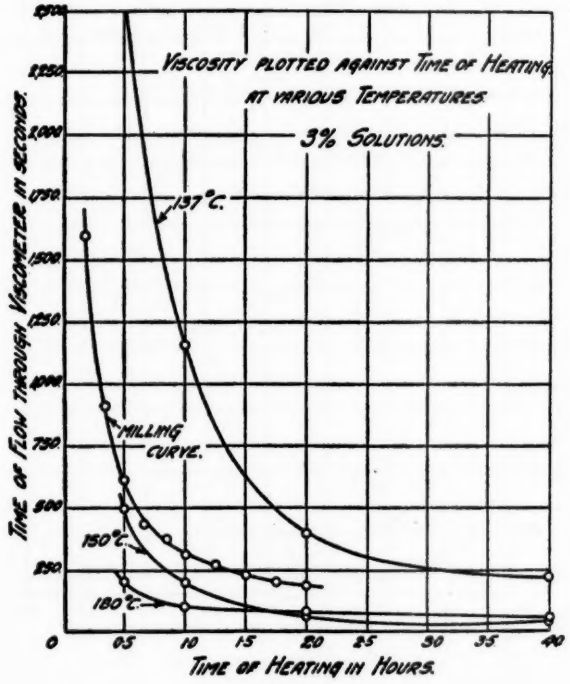

Figure 1

characterized by a rapid fall in the viscosity during the initial period, followed by a second stage in which comparatively little alteration takes place in the rubber so far as this particular property is concerned.

For the purpose of comparison the values obtained in the milling test have been included in Graphs 1 and 2, illustrating the effects produced by heat treatment alone. From these it will be apparent that while these changes are comparatively slight at temperatures in the neighborhood of 100° C., the effect rapidly increases with rise in temperature until at about 150° C. the curve connecting solution viscosity with time of heating closely approximates the corresponding curve for time of milling. It therefore seems probable that of the various changes produced in rubber by masticating or milling, the one associated with the marked

fall in solution viscosity is primarily due to the heat developed in the process and might be reproduced in technical practice by merely exposing the rubber to a temperature of 150° C. for a few hours.

The experiments so far described, however, had been carried out in the presence of air, and the question had still to be settled as to whether heat alone would bring about the observed changes. The curves themselves were of an exponential nature resembling those of a chemical action proceeding more rapidly at higher temperatures and falling off as the quantities of the reacting constituents diminished. This, taken in conjunction with the well-known fact that the oxidation

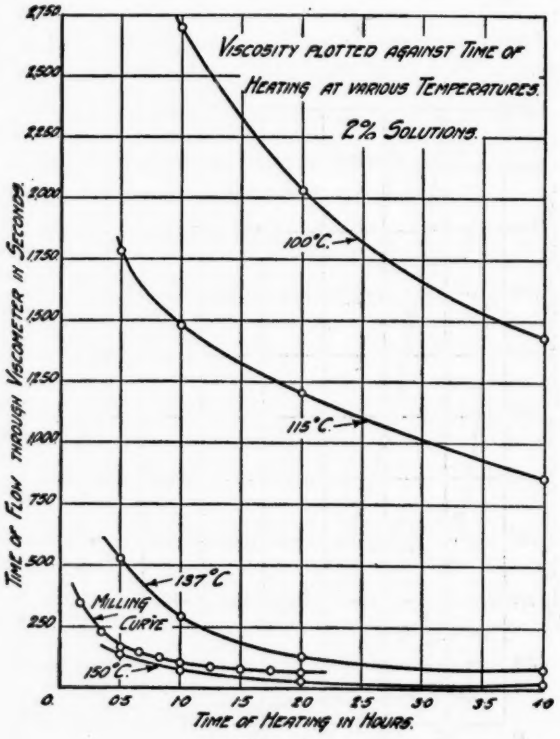

Figure 2

or perishing of raw rubber is usually associated with a low solution viscosity, gave rise to the assumption that oxygen as well as heat might be responsible for the changes taking place during milling. A preliminary experiment showed that such was the case.

A series of tubes containing weighed quantities of rubber was prepared as before, but prior to being heated, these were first connected to a Toepler pump, exhausted to a high degree, and while still connected, immersed in boiling water for an hour to remove as far as possible the air absorbed by the rubber and the walls of the tube. The tubes were then sealed off and treated in the same way as the first series, being subjected to the same range of temperatures for similar periods of time, and the contents of each afterwards made into a 2 per cent solution with benzene. On measuring the viscosities of the solutions it was found that very

little change had been brought about by the heating, and that even in the instance in which the rubber had been subjected to a temperature of 150° C. for 4 hours, the viscosity of the solution was very little lower than that of one of the same strength prepared from the untreated rubber. This may be judged from the following experimental data:

Period of heating, minutes	Viscosity	Previous result
30	Very great	141
60	Very great	77
120	Very great	33
240	2760	24

These striking observations were confirmed by a further set of experiments in which samples of rubber were heated at 150° C. for a period of 3 hours in atmos-

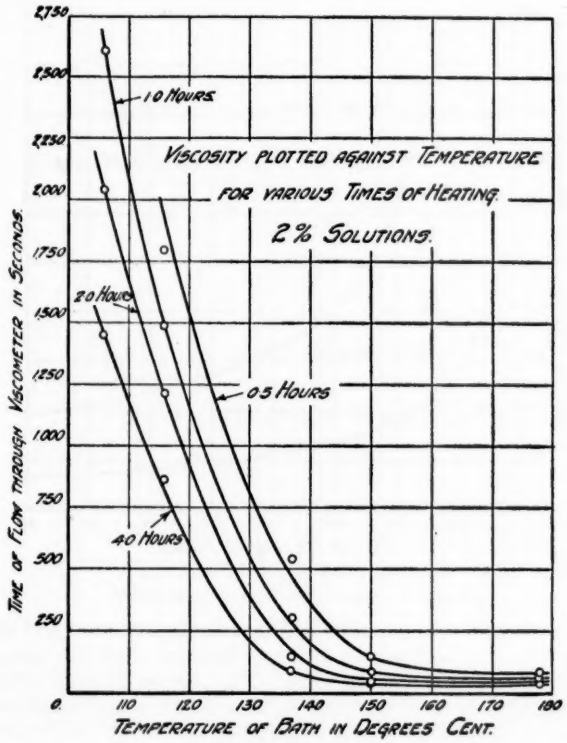

Figure 3

pheres of hydrogen, steam, and nitrogen, respectively, special precautions being taken in each instance to remove every trace of oxygen from the gas and to displace, first, all the air from the apparatus. The 2 per cent benzene solutions prepared from the samples after these treatments were found to be "stringy" in every instance, and the viscosities were again comparable with that of a solution made from the original rubber. The results clearly showed that the presence of oxygen was necessary before any marked reduction in solution viscosity could be brought about by heating rubber within the limits of temperature likely to arise in technical practice.

To amplify this conclusion and to determine whether any relation could be established between the change in solution viscosity and the quantity of oxygen present during the heat treatment, a further experiment was carried out in which samples of rubber were heated in sealed glass tubes containing varying known quantities of air. For this purpose a series of 5 tubes, each containing 1.0 g. of rubber, was connected to a Toepler pump and simultaneously exhausted, the removal of adsorbed air being assisted by immersing the tubes in boiling water during the operation. When the exhaustion of the tubes was complete, the temperature of the water-bath was adjusted to 15° C., and the tubes were sealed off in succession, the first at the stage of complete exhaustion, and the others in order after the readmission of a small quantity of air and the redetermination of the pressure in each instance. The sealed tubes were then subjected to a temperature

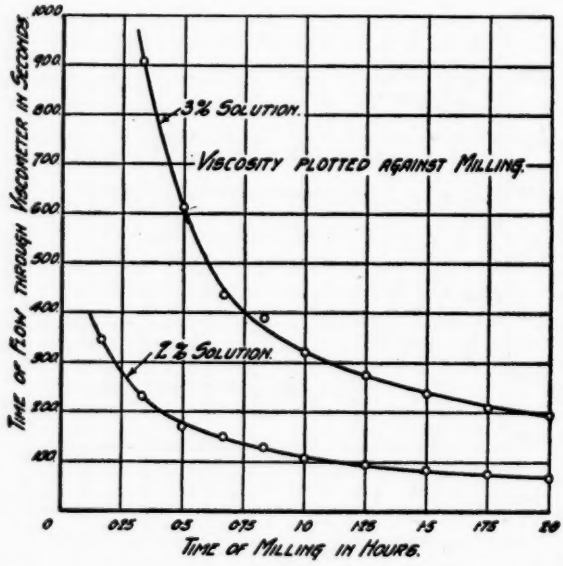

Figure 4

of 150° C. for 4 hours in the vapor of boiling anisole, removed and made up into a 1 per cent solution by addition to 99 cc. of benzene, and the viscosity was determined as in the previous experiments. The volume of each tube was subsequently determined, and from this and the temperature and pressure at which it was sealed, the oxygen content was calculated.

The following table shows the amount of oxygen present in each instance and the corresponding solution viscosity after heating:

No.	Weight of rubber	Oxygen added	Viscosity
1	1.0	0.000000	469
2	1.0	0.000046	393
3	1.0	0.000103	317
4	1.0	0.000491	160
5	1.0	0.000989	99

In addition, a separate test was carried out to determine the effect produced by the preliminary heating at 100° C., the effect produced by omitting this precau-

tion to remove the last traces of air, and the result obtained by heating the rubber in an unlimited supply of air.

Treatment	Oxygen present	Viscosity
(1) Open to air and heated at 150° C. for 4 hours	Unlimited	57.6
(2) Exhausted without preliminary heating. Sealed and heated to 150° C. for 4 hours	0.0000	350
(3) Open to air and heated to 100° C. for ½ hour	Unlimited	740
(4) Unheated raw rubber	.....	948

From the foregoing results, shown graphically in Figures 5 and 6, it will be seen that the presence of an extremely small quantity of oxygen is sufficient to bring

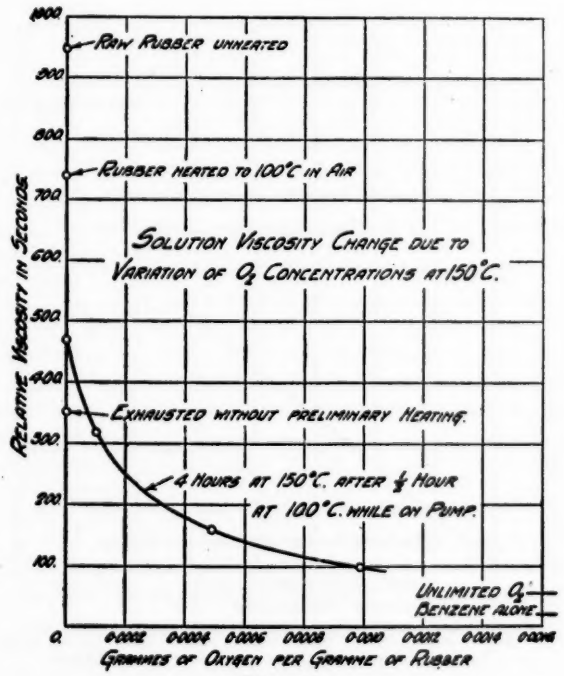

Figure 5

about a marked decrease in the solution viscosity when rubber is heated to temperatures in the region of 150° C., and that the fluidity of the solutions is within limits proportional to the weight of available oxygen present during the treatment.

The results of the investigation may now be summarized as follow:

(1) Heating raw rubber in the presence of air brings about a definite lowering of the solution viscosity, the extent of which depends on the temperature employed, and on the duration of the heating.

(2) Raw rubber may be heated in a vacuum to a temperature of 150° C. without any marked effect on its solution viscosity, provided that special precautions are taken to remove the last traces of oxygen.

(3) Raw rubber may be heated in an atmosphere of steam, hydrogen, or nitrogen to a temperature of 150° C. without any marked effect on its solution viscosity.

(4) Heating raw rubber in the presence of oxygen produces a marked decrease in the solution viscosity, and a relation has been established under certain conditions between the quantity of oxygen present per g. of rubber and the fluidity of the solutions.

(5) The effect produced by milling, so far as this is indicated by solution viscosity, can be imitated by heating rubber in the presence of oxygen or air.

(6) It would appear that the marked changes in solution viscosity produced by milling rubber or heating it in air are due to some chemical action in which oxygen takes part.

To sum up, the experiments described prove that heat and oxygen play an

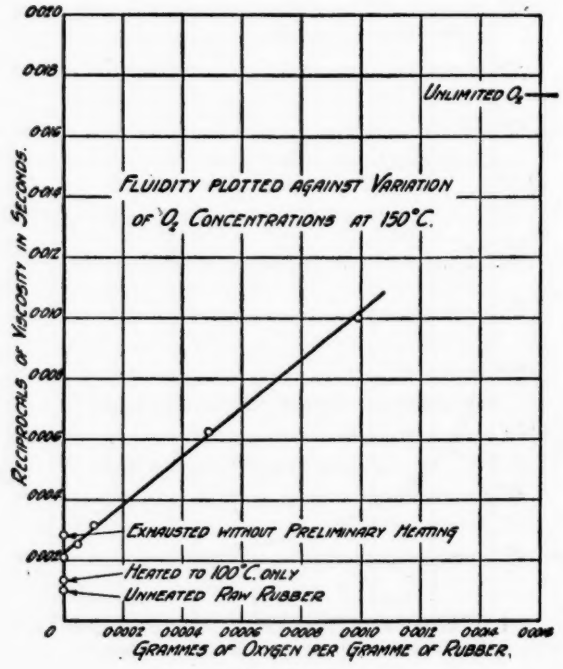

Figure 6

essential part in the milling process, and that so far as the properties indicated by solution viscosity are concerned, the effect of milling might be reproduced by a heat treatment. It must not be assumed from this, however, that mastication or milling is a simple process involving merely the combined action of heat and oxygen, and it is questionable whether such a treatment would reproduce all the effects of ordinary technical practice.

Further investigation is required before the nature of the changes which occur in rubber during milling are completely understood, and, for that matter, the mechanism of the action of heat and oxygen in reducing the solution viscosity. It has thus been shown that oxygen, hitherto regarded as the enemy of rubber. is in one process at least an important ally.

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The Reactions of Aniline and Its Homologs as Accelerators of Vulcanization

Takeo Kimishima

Reactions of Aniline as an Accelerator

The Plan of the Research

The accelerating action of aniline and its homologs can be considered from two points of view. The one is whether there are exothermic phenomena caused by the accelerators and the effect of those phenomena upon vulcanization. The other is the chemical effect upon vulcanization caused by reaction products derived as a result of chemical reaction of an accelerator and sulfur. In other words, the object of consideration in the former is the effect of thermal change, while that in the latter is the effect caused by chemical change.

Leaving the former for later discussion, the writer will first describe the result of his experiments concerning the reaction products of accelerators and sulfur and the effect of these products upon vulcanization.

In an investigation of this kind it is extremely difficult to extract and determine the effective elements from material derived from an accelerator in the process of vulcanizing reactions of rubber. No case has yet been known where a satisfactory result was realized by such a method.

Therefore, the writer has first taken up the investigations of reactions of an accelerator with sulfur and by separating and refining each of the various reaction products approached the matter of vulcanization itself, and under various conditions caused these reaction products to act upon rubber. Thus the writer has followed the plan of establishing the reaction mechanism of accelerators by seeing the changes, both chemical and physical, together with their effect upon vulcanization.

The Reaction Product of Aniline and Sulfur

Of the studies on the reaction product of aniline and sulfur the study of thioaniline by Merz and Weith (*Ber.*, 4 (1871), 384), the study of K. A. Hofmann (*Ber.* (1894), 2807, 3320) and the investigation of R. Nietzki and H. Bothof (*Ber.* (1894), 3261; (1896), 2774) can be given as references. Together with the above references, the experiments made by the writer show that when aniline and sulfur are heated for some hours at a temperature of 150° C. and caused to react, there will be seen *o*-diaminophenyldisulfide and a large quantity of hydrogen sulfide appearing as a reaction product, and at the same time a small quantity of *o*-diaminophenylmonosulfide and a large quantity of resinous substance containing a large quantity of sulfur in its elements.

The formation of these three products may be shown as follows:

$$2C_6H_5NH_2 + 3S \longrightarrow NH_2C_6H_4.S_2.C_6H_4NH_2 + H_2S$$
$$NH_2C_6H_4.S_2.C_6H_4NH_2 \longrightarrow NH_2.C_6H_4.S.C_6H_4.NH_2 + S$$

As shown in the foregoing formula, we have proved that aniline produces its disulfide which, when heated, will dissolve and change into monosulfide.

About the position of the amino group of the above-mentioned sulfide, Hofmann stated that it is in the *ortho* position, while Nietzki holds it to be the *para* compound, holding different opinions between them. The experiments made by various authorities, however, favor the theory of Hofmann, with whom the writer also agrees.

By heating a mixture of aniline and sulfur in an oil-bath at 160–170° C. and by using Hofmann's method the writer succeeded in separating from the reaction products a large quantity of *o*-diaminophenyldisulfide, with melting point of 95° C. (yellow slab-like crystals) and at the same time a small quantity of *o*-diaminophenylmonosulfide (white needle-like crystals), with melting point of 105° C.

But the writer, while in the process of separating and refining the above-mentioned disulfide, found a crystal compound of different shape coexisting with the other elements, and by carefully gathering those parts and recrystallizing and refining obtained yellowish needle-shaped crystals, having a melting point of 78° C.

To collect a large quantity of these crystals, reaction products of aniline and sulfur were dissolved in dilute HCl (four or five per cent concentration) and fractional neutralization was effected by the use of a caustic soda solution; thus as the first fraction a precipitate was obtained having *o*-diaminophenyldisulfide as its essential component, and then by perfectly neutralizing the filtrate thus secured by the use of a caustic soda solution, another precipitate was obtained having as its essence the above-mentioned base. For the refining of the base it is converted into hydrochloride and crystallized, the crystals are dissolved in twenty per cent alcohol, neutralized again to obtain a free base, which appears to be needle-shaped crystals of a straw color. The yield varies according to heating conditions. Moreover, the separation and the refining cannot be carried out satisfactorily, so the yield cannot be definitely ascertained. However, compared with *o*-diaminophenyldisulfide, the percentage yield is extremely small, not more than 10 per cent. If this free base is refined by recrystallizing several times, it will become needle-shaped crystals of almost white color, with melting point of 78° C. The percentage of each element in these crystals, obtained as the result of elemental analysis, is as mentioned below. In comparing this result with the calculated percentage of the element of diaminophenyldisulfide, $[(C_6H_4)NH_2S]_2$, a very close similarity is noticed between the two.

	The result of analysis of the sample (percentage)	Calculated no. of $[(C_6H_4)NH_2S]_2$ (percentage)
Carbon	58.23	58.03
Hydrogen	4.64	4.87
Nitrogen	11.30	11.28
Sulfur	26.15	25.82

The writer, assuming that this compound must be *p*-diaminophenyldisulfide, sought authorities as to its melting point and found that some say 78° C. and others 80° C. Among these different opinions, Hofmann's record shows it to be 80° C., a difference of 2° C. between it and the melting point of the compound found by the writer. But its hydrochloride is found to take the similar form of groups of fine white needles. The alcoholic solution of these crystals with addition of lead peroxide shows a maroon color. If heated with concentrated HCl, they show a purple color, which, diluted in water, will again turn into a purple-red color. All this behavior closely resembles that of *p*-diaminophenyldisulfide as recorded by Hofmann (*Ber.* (1894), 2813).

Thus, by the above-mentioned method of Hofmann, the writer prepared *p*-diaminophenyldisulfide, to determine the melting point, which proved to be 78° C. By mixing this with the crystals of the aforesaid compound, the writer again tried to determine the melting point, and found that there was no change. Therefore

it is concluded that the crystals separated previously from the *o*-diaminophenyldisulfide are *p*-diaminophenyldisulfide.

As has been previously stated, among the reaction products of aniline-sulfur, there coexists, besides those three kinds of crystals stated above, some resinous substance which is hard to crystallize and which is combined with a large quantity of sulfur. This resinous substance, after the aniline residue has been driven off by means of steam-distillation from the melt, was extracted with hydrochloric acid, and after removal of the hydrochloric acid, was subjected repeatedly with alcohol to the hot extraction of diaminophenyldisulfide and -monosulfide until the extract became colorless. It was again subjected to hot extraction of the undissolved portion by means of acetone. By the last extraction, a greater part of the resin dissolved in the solvent. Then this solution was evaporated to dryness with the vacuum evaporator, and a brittle resinous substance of glassy black color was secured. To this substance many methods were applied in order to get crystals, but without success.

The resinous substance had the percentage composition shown in the table below, an almost similar percentage to that of $C_{12}H_{12}N_2S_5$:

	Elements of resinous substance (experimental no.)	Elements of $C_{12}H_{12}N_2S_5$ (calculated no.)
Carbon	44.1	41.8
Hydrogen	3.9	3.5
Nitrogen	7.3	8.1
Sulfur	44.9	46.5

In the above comparison there is considerable agreement between the elements of both, roughly considered as a similar percentage composition. The resinous substance cannot be separated and refined as crystals and though there may be a closer agreement between the two it cannot immediately be concluded to be pentasulfide. Yet this material will serve as a confirmation, at least, of the existence of a polysulfide compound in the reaction product of aniline and sulfur. It is therefore proper to imagine that the resinous substance is composed mainly of pentasulfide, as well as of several kinds of polysulfide.

To recapitulate, the main reaction product of aniline and sulfur is *o*-diaminophenyldisulfide, and at the same time a large quantity of hydrogen-sulfide is obtained. Besides these, there appear a small quantity of *p*-diaminophenyldisulfide, a resinous substance which is supposed to be polysulfide and a certain quantity of monosulfide obtainable by thermal decomposition of *o*-diaminophenyldisulfide.

The result mentioned above is obtained by heating for a comparatively long time the mixture of aniline and sulfur in heat of a higher temperature than that of vulcanization. However, in the practical use of aniline as an accelerator, it will be noted that when the heating time is short, only a small part of the aniline changes into *o*-diaminophenyldisulfide and the production of other compounds can hardly be detected.

For the reasons stated so far, it can be seen that among the reaction products of aniline and sulfur, that which affects the vulcanization most is *o*-diaminophenyldisulfide; while other compounds may have some effect upon the vulcanization, such effect is very small compared with that of the former.

The writer tried to consider next the effects of *o*-diaminophenyldisulfide and other reaction products upon vulcanization.

The Effects of Reaction Products upon Vulcanization

There are many methods used in comparing the velocity of vulcanization of rubber. The sample can be heated and the change of its physical nature can be

noted. For instance, the time required to reach the state of correct cure may be determined. In this way the speed of vulcanization may be practically compared. But it is believed that for the purpose of the present research it will be altogether reasonable and convenient to determine the combined sulfur of the sample produced as the result of vulcanization and compare the quantity under the same condition. It is especially appropriate in that because by this means a quantitative comparison can be made from time to time.

The writer prepared a lot of pale crepe of stable quality and pure sulfur refined by recrystallization of stick sulfur; 92.5% of pale crepe and 7.5% of the powdered sulfur were mixed and a control mixture made. Against this in order to test the accelerating effect of aniline, 1% of aniline was added to the 100% of control mixture. And again, assuming the case where 1% aniline is converted entirely to sulfide by combination with sulfur, a mixture of 1.34% of *o*-diaminophenyldisulfide was made. By heating the above three kinds of mixtures under the same conditions, the degree of vulcanization of each mixture was compared.

In a test of this kind the rubber to be the ideal material should be chemically pure, free from resin and protein. But as a matter of practical fact, there is no way of obtaining a colloidal substance like rubber in a perfectly pure condition. Furthermore, even by using the method of Harries, which is considered to be the best refining method, all parts of refined rubber do not always show the same nature. Again if we consider the oxidation and deterioration after refining, there is much room for doubt as to the effect of refining.

Therefore avoiding this trouble, the writer used, as the case of Kratz (*J. Ind. Eng. Chem.* (1920), 317; (1921), 69), pale crepe of stable quality from beginning to end. In order to compare the effect of aniline and other accelerators, using the abovementioned mixture, the writer noted the difference between the coefficient of vulcanization of the mixture to which accelerators have been added with the coefficient of the control mixture, and called the differences as an excess sulfur coefficient. If the effects of the accelerators are compared in this way by the excess sulfur coefficient, the effect of impurity in the rubber mixture may be avoided to a certain extent.

The rubber material used was pure white, pale crepe, with moisture content of 0.87%, acetone extract 3.24%, and nitrogen content 0.74%.

The sulfur used was refined especially by recrystallization, because the sublimed sulfur usually found in the market contains some quantity of sulfurous acid and when vulcanization is effected in hydrogen sulfide, it will react with it.

The proportions of the mixture of the materials used in the vulcanization test are as follows:

Sample No.	Rubber	Sulfur	Aniline	*o*-Diamino-phenyldisulfide
1	92.5	7.5	0	0
2	92.5	7.5	1.0	0
3	92.5	7.5	0	1.34

The mixing was done under the same conditions by means of an experimental mixing mill for 30–35 minutes. During the latter half of the mixing, cold water was run through the mill to keep the temperature of the mixture under 50° C.

The experimental mixture was made into slab form, 2 mm. thick, 40 mm. wide, and 55 mm. long and placed in the heating chamber in an oil-bath at a fixed temperature for a certain period, and thus the quantity of combined sulfur in the vulcanized rubber was determined.

In an oblong oil-bath with a stirrer, three heating chambers made of aluminum, 20 mm. wide, 2.5 mm. high, and 200 mm. long, were placed. This arrangement con-

stitutes a heating apparatus, so made that the mixture may be put on an aluminum plate and inserted through an opening which may be closed at once. In the heating chamber, two small delivery tubes were attached through which the desired quantity of gas was conducted. The outside of the oil-bath was wrapped with asbestos to conserve the heat, and in order to heat the bath a Bunsen burner with a pressure governor was used, and this was supplemented by a smaller burner, the flame of which could be easily controlled. Thus the oil-bath was successfully kept at an even temperature with an experimental error of less than 0.5° C.

The temperature of the heating chamber chosen as most suitable for the vulcanization test was 140–150° C. For the purpose of keeping the temperature within this limit the temperature of the oil-bath was fixed at 145° C.

The analysis of the vulcanized mixture, e. g., the determination of the acetone extract and of combined sulfur, was made in accordance with the method of the American Bureau of Standards (Circular of the Bureau of Standards, U. S. A., No. 38, "The Testing of Rubber Goods"). Then dividing the quantity of combined sulfur by the remainder of the weight of vulcanized sample after the quantity of acetone extract and of combined sulfur has been deducted, and multiplying the quotient thus obtained by 100 the vulcanization coefficient was obtained.

The vulcanization test was at first limited to the heating of the mixture in the heating chamber with air. In this case the mixture with *o*-diaminophenyldisulfide did not show any especial acceleration in vulcanization. On the other hand in the actual reaction of aniline and sulfur together with production of *o*-diaminophenyldisulfide a large quantity of hydrogen sulfide is produced. In view of this fact it was noted that the coexistence of the sulfides with hydrogen sulfide may have an important bearing upon the vulcanization mechanism, and consequently the mixture was heated in the heating chamber with hydrogen sulfide gas, and finally the effect of the vulcanizing action noted; thus the starting point of the reaction mechanism of aniline was arrived at.

On the other hand a base with a constitution like diaminophenyldisulfide has a general tendency to be decomposed by heat. When the mixture containing this kind of accelerator is heated in the air it is doubtful whether it will show the real effect on vulcanization without decomposing by oxidation. Owing to this doubt, the mixture was heated in an inert gas which would prevent oxidation, for instance carbon dioxide or nitrogen. It was felt necessary to consider these three cases of action in analyzing the effect of accelerator.

Regarding three mixtures mentioned above, the vulcanizing test was made under the three conditions, and by obtaining the excess-sulfur coefficient in case any accelerator was added. The results were then compared. The following is the result of the test:

TABLE 1

COEFFICIENT OF (1) SAMPLE MIXTURE (COMPOSITION 1)

(A) When heated in the air

The temperature of oil-bath, ° C.	Heating duration, min.	Acetone extract, %	Combined sulfur, %	Vulcanization coefficient
145	15	9.48	0.67	0.75
145	30	9.31	0.88	0.98
145	45	9.13	1.18	1.32
145	60	8.80	1.54	1.72

(B) When heated in inert gas (carbon dioxide)

The temperature of oil-bath, ° C.	Heating duration, min.	Acetone extract, %	Combined sulfur, %	Vulcanization coefficient
145	15	9.62	0.71	0.79
145	30	9.26	1.03	1.15
145	45	8.89	1.47	1.64
145	60	8.42	1.88	2.10

(C) When heated in hydrogen sulfide

The temperature of oil-bath, ° C.	Heating duration, min.	Acetone extract, %	Combined sulfur, %	Vulcanization coefficient
145	15	9.42	0.78	0.87
145	30	9.20	1.12	1.25
145	45	8.77	1.61	1.80
145	60	8.13	2.22	2.48

It is noted from the above results that the coefficient of vulcanization of the sample mixture shows some difference in oxidizing, neutral, and reducing atmospheres. This may be considered to be due to the effect upon the vulcanization, caused chiefly by the different action in each of the atmospheres, of impurities, especially protein, contained in the rubber.

[Since in the preliminary test the result of vulcanization on the rubber free from resin showed a tendency similar to that of Table 1 of the above three cases (A), (B), and (C), and also in the test on the mixture free from resin and protein the coefficient of vulcanization in the case of (A) is somewhat lower than the others, whereas both (B) and (C) show similar values in their coefficient of vulcanization, therefore it may be presumed that the above difference was produced by the action of nitrogenous compound on the hydrogen sulfide.]

(2) MIXTURE, VULCANIZATION TEST NO. 2 (VULCANIZATION ACTION OF ANILINE)

(A) When heated in the air (oil-bath 145° C.)

Heating duration, min.	Acetone extract, %	Sulfur combined, %	Coef. of vul.	Standard coef. of vul.	Excess S coef.
15	9.80	0.67	0.75	0.75	+0
30	9.11	1.14	1.27	0.98	+0.29
45	8.67	1.64	1.83	1.32	+0.51
60	8.06	2.24	2.50	1.72	+0.78

(B) When heated in inert gas (carbon dioxide) (oil bath same temp.)

Heating duration, min.	Acetone extract, %	Sulfur combined, %	Coef. of vul.	Standard coef. of vul.	Excess S coef.
15	9.90	0.73	0.82	0.79	+0.03
30	9.15	1.32	1.47	1.15	+0.32
45	8.59	1.97	2.20	1.64	+0.56
60	8.06	2.52	2.82	2.10	+0.72

(C) When heated in hydrogen sulfide (same temperature)

Heating duration, min.	Acetone extract, %	Sulfur combined, %	Coef. of vul.	Standard coef. of vul.	Excess S coef.
15	9.88	0.81	0.91	0.87	+0.04
30	9.17	1.21	1.35	1.25	+0.10
45	8.53	1.82	2.03	1.80	+0.23
60	8.03	2.44	2.73	2.48	+0.25

(3) MIXTURE VULCANIZATION TEST NO. 3 (RESULTS OF VULCANIZATION OF *o*-DIAMINOPHENYLDISULFIDE-RUBBER COMPOUND)

(A) When heated in the air (same temperature)

Heating duration, min.	Acetone extract, %	Sulfur combined, %	Coef. of vul.	Standard coef. of vul.	Excess S coef.
15	10.57	0.73	0.82	0.75	+0.07
30	10.05	1.04	1.17	0.98	+0.19
45	9.67	1.44	16.2	1.32	+0.30
60	8.97	1.94	2.17	1.72	+0.45

(B) When heated in inert gas (same temperature)

Heating duration, min.	Acetone extract, %	Sulfur combined, %	Coef. of vul.	Standard coef. of vul.	Excess S coef.
15	10.55	0.76	0.86	0.79	+0.07
30	9.75	1.25	1.40	1.15	+0.25
45	9.30	1.81	2.04	1.64	+0.40
60	8.53	2.38	2.67	2.10	+0.57

(C) When heated in hydrogen sulfide (same temperature)

Heating duration, min.	Acetone extract, %	Sulfur combined, %	Coef. of vul.	Standard coef. of vul.	Excess S coef.
15	10.18	1.29	1.46	0.87	+0.59
30	9.62	2.15	2.44	1.25	+1.19
45	8.95	2.98	3.38	1.80	+1.58
60	7.80	4.02	4.56	2.48	+2.08

In comparing the excess sulfur coefficient of the samples of (2) and (3) of the above table, we note that whereas the vulcanization coefficients of the mixtures of (A) and (B) of (2) are slightly greater than those of (A) and (B) of (3), the excess sulfur coefficient of (C) of mixture (3) is much larger than that of mixture (2). Moreover it is noted that the excess sulfur coefficient of (C) is four- to five-fold greater than that of (A) and (B) of the mixture (3). This fact indicates clearly that there must exist some mechanism of vulcanization between *o*-diaminophenyldisulfide and hydrogen sulfide.

Now in pursuing the reactions which may exist between the disulfide and H_2S, the reduction of the disulfide by hydrogen sulfide will, first of all, be imagined. If a stream of H_2S gas is passed for a long time into an acidic solution of *o*-diaminophenyldisulfide which is kept hot on the water-bath, there occurs a phenomenon showing that the disulfide can be easily reduced to *o*-aminothiophenol, separating the free sulfur as a precipitate. The relation can be seen by the following chemical equation:

$$NH_2 \cdot C_6H_4 \cdot S \cdot S \cdot C_6H_4 \cdot NH_2 + H_2S = 2NH_2 \cdot C_6H_4 \cdot SH + S$$

After the separation of sulfur crystals, the neutralized solution of *o*-aminothiophenol can be oxidized again by letting the solution stand in air or introducing an air current into it to accelerate the oxidizing reaction; this again results in the gradual appearance of some fine yellow crystals of *o*-diaminophenyldisulfide from the solution. In the same manner, *o*-aminothiophenol can be oxidized to disulfide by fusing it together with sulfur. Basing on this fact, the explanation of the reactions of aniline as an accelerator may be made as follows.

o-Diaminophenyldisulfide, the reaction product of aniline and sulfur, is reduced to *o*-aminothiophenol by H_2S, and simultaneously reacts, giving active sulfur (or nascent state of S) to rubber; whereas the reduced aminothiophenol is oxidized again by sulfur so as to reproduce disulfide and hydrogen sulfide. Thus repeating these reactions in cycle, the rubber will be vulcanized to the state of correct cure by the action of so-called active sulfur.

In order to confirm the truth of this hypothesis, one should have experimental support, demonstrating not only that rubber can be vulcanized with *o*-diaminophenyldisulfide and hydrogen sulfide alone but also that aminothiophenol is the active element in the acceleration.

As a test of the former, 100 parts of rubber were mixed with 23.25 parts of *o*-diaminophenyldisulfide, and the slabs heated in an H_2S atmosphere. If the disulfide so compounded is totally reduced by H_2S, it will give about 3% of active sulfur on the rubber, aiding in obtaining the "correct cure."

As a parallel test the same sample material was heated in an inert gas, the result of which is seen in the following table:

TABLE 2

VULCANIZING TEST OF RUBBER WITH *o*-DIAMINOPHENYLDISULFIDE AND HYDROGEN SULFIDE

(A) Heating the rubber compounds in H_2S atmosphere

Temperature, ° C.	Time of heating, min.	Acetone ext., %	Combined S, %	Coef. of vul.
145	20	16.8	1.04	1.27
145	40	15.6	1.16	1.39
145	60	14.3	1.27	1.50

(B) Heating the samples in an inert gas (nitrogen)

Temperature, ° C.	Time of heating, min.	Acetone ext., %	Combined S, %	Coef. of vul.
145	20	19.9	0.54	0.68
145	40	19.0	0.88	1.10
145	60	18.2	1.11	1.38

All the samples vulcanized in (B) were sticky, in a state of so-called "undercure." In (A), the first two heated 20 min. and 40 min., respectively, were sticky, so that the physical property was nearly the same as that of (B), while the last one in (A) heated for 60 min. in H_2S had nearly reached the state of "correct cure." In this test it is noted that the rubber can hardly be vulcanized with *o*-diaminophenyldisulfide and H_2S only.

As a conceivable explanation of this fact, one may mention the solvent-action of aminothiophenol, which has a melting point as low as 26° C., on rubber and sulfur, because it is a well-known fact that the vulcanizing velocity of rubber in solution is greatly decreased by the effect of the rubber solvents.

Effect of *o*-Aminothiophenol as an Accelerator of Vulcanization

To prepare a pure *o*-aminothiophenol, *o*-diaminophenyldisulfide is reduced with metallic tin in dilute acid solution. After the reduction process is completed with hydrogen, the hydrochloride of aminothiophenol is isolated by condensation in the form of white crystals. These crystals are dissolved in water and neutralized by caustic soda, giving the free base. When the crude product thus secured is distilled in a vacuum, and the distillate is cooled, pure needle-shaped crystals with melting point 26° C. are obtained.

But it must be remembered that *o*-aminothiophenol is a compound easily oxidizable in air to the original disulfide. Consequently, the mixing with rubber cannot be done by the ordinary means of milling. The writer, in order to prevent the oxidation, preferred the very tedious way, i. e., mixing the material in the form of solution in hydrogen atmosphere and preparing slab samples by clearing the solvent off in a vacuum. The composition of the compound is 1.34 parts of *o*-aminothiophenol in 100 parts of rubber-S mixture. The control mixtures for the parallel test were also made by the same process. These two kinds of samples made in this

manner are cured in an inert gas to demonstrate the action of the aminothiophenol as an accelerator on vulcanization. The results are as follows:

TABLE 3

THE EFFECT OF AMINOTHIOPHENOL (*o*) ON VULCANIZATION HEATING THE COMPOUNDS IN AN INERT GAS (145° C.)

Time of heating, min.	Acetone ext., %	Combined S, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	9.42	1.45	1.62	0.83	+0.79
30	8.97	2.30	2.59	1.14	+1.45
45	7.98	3.45	3.89	1.51	+2.38
60	7.02	4.23	4.77	1.86	+2.91

The action of *o*-aminothiophenol thus measured by their excess-sulfur-coefficient is of the same grade as that of *o*-diaminophenyldisulfide in H_2S gas, which is given in Table 2.

Then the course of oxidation by sulfur of *o*-aminothiophenol to the corresponding disulfide becomes an important subject for further investigation. Naturally two courses may be imagined, the one is a direct formation of disulfide from aminothiophenol and sulfur; and the other is to assume an intermediate formation of polysulfide, which is decomposed by heat to disulfide and active sulfur as the final products. These courses are evident in the following equations:

$$2NH_2{\cdot}C_6H_4SH + S = (NH_2{\cdot}C_6H_4)_2S_2 + H_2S \quad (1)$$
$$2NH_2{\cdot}C_6H_4{\cdot}SH + XS = (NH_2{\cdot}C_6H_4)_2S_{(X+1)} + H_2S \quad (2)$$
$$(NH_2{\cdot}C_6H_4)_2S_{(X+1)} = (NH_2{\cdot}C_6H_4)_2S_2 + (X - 1)S \quad (3)$$

Now the hypothesis of polysulfide-formation is strengthened by the separation of resinous polysulfide from aniline-sulfur melt, a fact already mentioned in this paper.

In addition to the above, the study of ammonium polysulfide by Thomas and Riding (*J. Chem. Soc.* (1923), 729, 1726) confirms the formation of pentasulfide as an intermediate product in the disulfide formation from NH_4SH and sulfur. The study of the reaction of *m*-tolylenediamine and sulfur by Schultz and Bayschlag (*Ber.*, 42, 743 (1909)) which revealed the occurrence of polysulfide as the reaction product also supports the hypothesis to some extent.

If the polysulfide formation and its decomposition to active sulfur and disulfide is assumed, the sulfur which is set free must have some influence on the rubber as in the case of Peachy's vulcanization.

As an experimental proof of the effect of polysulfide on vulcanization, the action of *o*-aminothiophenol with equimolecular quantities of sulfur to form various sulfides—from the higher polysulfide to the lower monosulfide—was determined with the samples the composition of which is seen below:

No. of sample	Rubber, parts	S, parts	*o*-Aminothiophenol	Mol. proportion of thiophenol to S
1	92.5	7.5	1.35	1:22.2
2	92.5	7.5	22.00	1: 1.36
3	92.5	7.5	58.20	1: 0.50
4	92.5	22.5	22.00	1: 4.10
5	92.5	30.0	58.20	1: 2.05

As already discussed the action of aminothiophenol was greatly influenced by the proportion of sulfur added; the results are shown in Table 4.

TABLE 4

(A) Coefficient of vulcanization and excess S coefficient of the sample No. 1. (temp. of the oil-bath, 147° C.)

Time of heating, min.	Acetone ext., %	Combined S, %	Coef. of vul.	C. V. control mix.	Excess S coef.
20	8.23	3.52	3.98	2.57	+1.41
40	7.40	5.15	5.89	3.36	+2.53
60	6.70	6.72	7.76	4.08	+3.68

(B) Coefficient of vulcanization and excess S coefficient of the sample No. 2. (temp. of the oil-bath, 147° C.)

Time of heating, min.	Acetone ext., %	Combined S, %	Coef. of vul.	C. V. control mix.	Excess S coef.
20	21.1	3.45	4.56	2.57	+1.99
40	19.6	5.08	6.74	3.36	+3.38
60	17.3	5.73	7.44	4.08	+3.36

(C) Coefficient of vulcanization and excess S coefficient of the sample No. 3 (temp. of the oil-bath, 147° C.)

Time of heating, min.	Acetone ext., %	Combined S, %	Coef. of vul.	C. V. control mix.	Excess S coef.
20	43.1	1.00	1.79	2.57	−0.78
40	41.96	1.60	2.83	3.36	−0.53
60	42.01	1.99	3.55	4.08	−0.53

(D) Coefficient of vulcanization and excess S coefficient of the sample No. 4 (temp. of the oil-bath, 147° C.)

Time of heating, min.	Acetone ext., %	Combined S, %	Coef. of vul.	C. V. control mix.	Excess S coef.
20	25.7	6.03	8.83	4.66	+ 4.17
40	13.9	14.20	19.8	7.08	+12.7
60	13.2	15.40	21.6	8.42	+13.2

(E) Coefficient of vulcanization and excess S coefficient of the sample No. 5 (temp. of the oil-bath, 147° C.)

Time of heating, min.	Acetone ext., %	Combined S, %	Coef. of vul.	C. V. control mix.	Excess S coef.
20	47.7	2.45	4.92	3.67	+1.25
40	44.6	5.22	10.40	6.65	+3.75
60	40.2	7.34	13.98	8.69	+5.29

By the data given above, it is evident that the excess S coeffs. of samples No. 1 and No. 2 are nearly equal in magnitude, but the action produced by the same quantity of aminothiophenol is ten-fold greater in the former case than in the latter.

Similarly the action of aminothiophenol is greater in No. 4 than that in No. 2 and less than that in No. 1. In these cases aminothiophenol reacts as an accelerator to enhance the velocity of vulcanization. On the contrary, aminothiophenol contained in sample No. 3 reacts as a negative accelerator with a retarding effect on the vulcanization; while in the case of No. 5, though the proportion of aminothiophenol to rubber is the same as in the case of No. 3, its excess S coefficients are positive owing to the greater proportion of sulfur added than was in the former case.

Generally speaking, it might be said that *o*-aminothiophenol reacts as a strong accelerator when it has a large quantity of sulfur, but if the amount of sulfur is decreased to a certain limit in its proportion, the action of the aminothiophenol

becomes zero, or it even retards the velocity of vulcanization as a negative accelerator.

These facts suggest to us the very important relation existing between the polysulfide formation and the mechanism of vulcanization.

Effect of Resinous Polysulfide on the Vulcanization of Rubber

As already mentioned, the action of *o*-aminothiophenol should be considered as a result of polysulfide formation with sulfur as its reaction mechanism. For the experimental support of this consideration, two tests are carried out. The one was the test on the effect of resinous polysulfide as an accelerator, which is isolated from an aniline-sulfur melt; the other was the vulcanizing test of rubber by polysulfide without any intermixture of sulfur.

The sample prepared for the former test had the following composition: 92.5 parts rubber, 7.5 parts sulfur, and 1.85 parts of resinous polysulfide. (Equivalent weight of polysulfide for one part of aniline is calculated assuming that it is the pentasulfide, whose 1.85 parts have 0.49 parts of sulfur to be set free.)

TABLE 5

EFFECT OF POLYSULFIDE AS AN ACCELERATOR OF VULCANIZATION

(A) When the compounds are heated in an inert gas (temp. of oil-bath, 145° C.)

Time of heating, min.	Acetone ext., %	Combined S, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	9.96	1.12	1.26	0.79	+0.47
30	9.73	1.60	1.81	1.15	+0.66
45	8.45	2.23	2.50	1.64	+0.86
60	8.26	2.96	3.33	2.10	+1.23

(B) When the compounds are heated in H_2S (temp. of oil-bath, 145° C.)

Time of heating, min.	Acetone ext., %	Combined S, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	10.15	1.28	1.45	0.87	+0.58
30	9.19	2.55	2.89	1.25	+1.64
45	8.14	3.23	3.64	1.80	+1.84
60	7.14	4.38	4.95	2.48	+2.47

As shown in the foregoing table, the accelerating action of the polysulfide and that of the disulfide (*o*-diaminophenyldisulfide) are nearly the same in degree, taking into consideration the active S which is set free by the thermal decomposition of the polysulfide.

Vulcanizing Test of the Polysulfide-Rubber Compound without Sulfur

The sample used in this test has the following composition: 100 parts of rubber; 11.5 parts of resinous polysulfide, isolated from aniline-S melt. In this case, the total amount of sulfur contained in 100 parts of rubber in the form of polysulfide is 5.16 parts, which sets free 3.1 parts of active sulfur by thermal decomposition, taking into account the fact that the polysulfide is a pentasulfide which decomposes to disulfide and S.

(C) When the polysulfide-rubber compounds are heated in H_2S (temp. of oil-bath, 145° C.)

Time of heating, min.	Acetone ext., %	Combined S, %	Coef. of vul.
20	12.45	1.53	1.78
40	11.10	2.21	2.55
60	10.37	2.67	3.07

By applying a thumb test to the physical properties of the cured compounds, it was found that the first of the test samples was in the state of "undercure," but that the other two samples had nearly reached the state of "correct cure." From the results discussed above, the reaction of aniline as an accelerator may be summarized as follows:

(1) Ortho-diaminophenyldisulfide, the reaction product of aniline and sulfur, reacts as a strong accelerator in collaboration with hydrogen sulfide.

(2) Ortho-aminothiophenol is produced by the reduction of the former disulfide with hydrogen sulfide. This compound acts strongly on vulcanization due to the active sulfur set free during the change of oxidation to the disulfide by sulfur, it being assumed that a temporary formation of polysulfide as an intermediate product takes place.

(3) The resinous polysulfide, isolated from aniline-sulfur melt, has a similar action on vulcanization as *o*-diaminophenyldisulfide has in the presence of hydrogen sulfide. If a sufficient quantity of the polysulfide is mixed with rubber, the rubber compound can be vulcanized to the state of "correct cure" without sulfur.

(4) In the reaction of the oxidation of *o*-aminothiophenol by sulfur, the unstable polysulfide formation may be assumed as already mentioned, because the resinous polysulfide can be actually found in aniline-sulfur melt and analogous examples of the formation of polysulfide are found in the literature of the subject, which also supports the reasonableness of this argument.

Taking these facts into consideration, a hypothesis is proposed by the writer for the reaction mechanism of aniline as an accelerator, which will give a reasonable explanation of the behavior of aniline. The reaction mechanism may be expressed in the following equations:

$$NH_2{\cdot}C_6H_5 + S = NH_2{\cdot}C_6H_4{\cdot}SH \quad (1)$$

$$2NH_2{\cdot}C_6H_4{\cdot}SH + XS = (NH_2{\cdot}C_6H_4)_2S_{(X+1)} + H_2S \quad (2)$$

$$(NH_2{\cdot}C_6H_4)_2S_{(X+1)} = (NH_2{\cdot}C_6H_4)_2S_2 + (X - 1)S \text{ (Active sulfur)} \quad (3)$$

$$(NH_2C_6H_4)_2S_2 + H_2S = 2NH_2C_6H_4{\cdot}SH + S \text{ (Active sulfur)} \quad (4)$$

There are two kinds of accelerators: the one is the organic base whose action on vulcanization can be obtained only with zinc oxide, e. g., thiocarbanilide and its kindred compounds, while the other is the accelerator the action of which on vulcanization can be obtained without ZnO. Aniline and its homologs belong to the second class and its action seems rather to be decreased by the presence of ZnO. This fact can be easily explained by the reaction mechanism in the above formula, because ZnO reacts generally as the absorbent of hydrogen sulfide during the reaction, so as to prevent the action of the disulfide accelerator. Moreover, the existence of ZnO in the aniline-S reaction tends to create a favorable condition for direct formation of the monosulfide, just as litharge does, the action of which is weaker than the disulfide in the presence of hydrogen sulfide. This fact will be seen later.

Among the products found in the aniline-sulfur melt, there are other sulfides which in association with *o*-diaminophenyldisulfide occur in small quantities, namely, *p*-diaminophenyldisulfide and *o*-diaminophenylmonosulfide. The yields of these compounds being small compared with those of the former disulfide, they have but little influence upon vulcanization. Still it is very important to ascertain their action on vulcanization with a view to discovering some new accelerators.

Next, as parallel experiments of the former test, the writer used rubber compounds of the composition mentioned below:

No. of sample	Rubber	Sulfur	Accelerator	Chemical name
1	92.5	7.5	1.34	*p*-Diaminophenyldisulfide
2	92.5	7.5	1.16	*o*-Diaminophenylmonosulfide

The quantity of the accelerators added was the equimolecular quantity of their respective sulfides, which can theoretically be derived from one part of aniline.

TABLE 6

THE ACTION OF *p*-DIAMINOPHENYLDISULFIDE AND *o*-DIAMINOPHENYLMONOSULFIDE AS AN ACCELERATOR OF VULCANIZATION

(1) *p*-Diaminophenyldisulfide as an accelerator

(A) When the compounds (No. 1) are heated in air (temp. of oil-bath, 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	9.77	1.38	1.55	0.75	+0.80
30	8.55	2.40	2.69	0.98	+1.71
45	7.63	3.16	3.54	1.32	+2.22
60	6.39	4.10	4.58	1.72	+2.86

(B) When the compounds are heated in an inert gas (CO_2) (temp. of oil-bath, 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	9.40	1.49	1.67	0.79	+0.88
30	8.50	2.48	2.78	1.15	+1.63
45	7.44	3.33	3.73	1.64	+2.09
60	6.47	4.42	4.96	2.10	+2.86

(C) When the compounds are heated in hydrogen sulfide (temp. of oil-bath, 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	9.19	1.91	2.15	0.87	+1.28
30	7.59	3.63	4.09	1.25	+2.84
45	6.18	4.94	5.56	1.80	+3.76
60	5.12	6.17	6.96	2.48	+4.48

(2) *o*-Diaminophenylmonosulfide as an accelerator

(A) When the compounds (No. 2) are heated in air (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	9.51	0.72	0.80	0.75	+0.05
30	8.89	1.07	1.19	0.98	+0.21
45	8.32	1.43	1.59	1.32	+0.27
60	7.64	2.00	2.21	1.72	+0.49

(B) When the compounds are heated in carbon dioxide gas (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	9.59	0.84	0.94	0.79	+0.15
30	8.98	1.26	1.40	1.15	+0.25
45	8.28	1.82	2.02	1.64	+0.38
60	7.62	2.49	2.77	2.10	+0.67

(C) When the compounds are heated in hydrogen sulfide (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	9.11	1.13	1.26	0.87	+0.39
30	8.55	1.63	1.82	1.27	+0.55
45	8.03	2.19	2.44	1.80	+0.64
60	7.26	3.01	3.35	2.48	+0.87

[REMARKS: The samples used in these experiments were stored in the vessel filled with the same kind of gas used in the heating chamber, so that the gas might be absorbed as much as possible before heating the samples. The absorption of hydrogen sulfide by rubber compounds is remarkable, i. e., 2.7 times the original volume of the rubber at the indoor temperature.]

In the result above mentioned, it is soon noticed that the action of *p*-diaminophenyldisulfide as an accelerator is greater than that of *o*-diaminophenyldisulfide in every case. Especially the property which is still effective on vulcanization without H_2S will be found useful as a new accelerator. But the reaction mechanism of *p*-diaminophenyldisulfide in this case is not certain. One possible explanation is the same as that of *o*-disulfide; in this case the hydrogen sulfide is in service as the reducing agent as imagined to occur by the reaction of sulfur on resin while heating the rubber-sulfur compounds, so the *p*-compound must be assumed a more easily reducible one than the *o*-compound in this explanation. The other mechanism is the unstable polysulfide formation resulting from thermal decomposition of the disulfide into two mols of the monosulfide with monovalent sulfur, which combines with sulfur to produce polysulfide and then giving off the active sulfur to the rubber. (Lecher, *Ber.*, 48 (1915), 524; (1920) 53, 577; and see also Stewart, "Recent Advances in Organic Chemistry," 1920, p. 309).

The action of *o*-diaminophenylmonosulfide on vulcanization is nearly equal to that of *o*-disulfide, in air or in CO_2 gas, while the power of the former as an accelerator in the presence of H_2S is far inferior to that of disulfide. This difference may be attributed to their reduced products, which point is verified by the following chemical equation:

$$(NH_2 \cdot C_6H_4)_2S + H_2S = 2NH_2 \cdot C_6H_5 + 2S$$
$$(NH_2 \cdot C_6H_4)_2S_2 + H_2S = 2NH_2 \cdot C_6H_4 \cdot SH + S$$

The valuation of these sulfides as an accelerator must be determined not only by the excess sulfur coefficient but also by the physical property of the vulcanized rubber compounds, such as the tensile strength at break or the percentage elongation, etc. These tests will be carried out afterwards.

The Reaction of Some Homologs of Aniline as Accelerators of Vulcanization

(1) Monomethylaniline and Dimethylaniline

Both of these compounds are weaker accelerators than aniline, and for that reason they are used very seldom in industry. As parallel experiments with those of aniline, equimolecular quantities of these accelerators corresponding to one part of aniline are compounded with 100 parts of rubber-sulfur compound, respectively. (The equimol. quantity of the former for 1 part of aniline is 1.15 parts, while that of the latter is 1.31 parts.) The compounding mixtures were heated in the same vulcanizing apparatus used in the case of aniline, keeping the temperature of the heating medium constant at 145° C.

Both of these accelerators used for the compounding were of the purest kind, and each of them had a boiling point of 193° C.

The results of this vulcanizing test are seen in Tables 7 and 8 given below:

TABLE 7

MONOMETHYLANILINE AS AN ACCELERATOR

(A) When the compounds are heated in air (temp. of oil-bath, 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	9.81	0.66	0.74	0.75	−0.01
30	9.50	0.93	1.04	0.98	+0.06
45	9.00	1.25	1.39	1.32	+0.07
60	8.57	1.65	1.84	1.72	+0.12

(B) When the compounds are heated in H_2S (temp. of oil-bath, 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	9.26	0.75	0.83	0.87	−0.04
30	9.16	1.15	1.28	1.25	+0.03
45	8.60	1.70	1.90	1.80	+0.10
60	8.04	2.33	2.60	2.48	+0.12

TABLE 8

DIMETHYLANILINE AS AN ACCELERATOR

(A) When the compounds are heated in air (temp. of oil-bath, 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	9.80	0.75	0.84	0.75	+0.09
30	9.15	1.03	1.15	0.98	+0.17
45	8.76	1.46	1.62	1.32	+0.30
60	8.12	2.02	2.25	1.72	+0.53

(B) When the compounds are heated in H_2S (temp. of oil-bath, 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	9.52	0.88	0.98	0.87	+0.11
30	8.85	1.33	1.48	1.25	+0.23
45	8.15	1.95	2.17	1.80	+0.37
60	7.61	2.69	3.00	2.48	+0.52

(Heating in an inert gas is omitted.)

In the tables given above it is observed that the effect of both these accelerators on vulcanization is very weak, especially in the case of monomethylaniline.

The Reaction Products of Monomethylaniline and Dimethylaniline on Sulfur

The study of the reaction products of dimethylaniline and sulfur was made by Möhlau and Krohn (*Ber.*, 21 (1888), 59–67).

When a mixture of these substances is heated at 200° C. for ten hours, the formation of two compounds, "methylaminophenylmercaptan" and "benzothiazolemethenesulfide," takes place, and at the same time a large quantity of hydrogen sulfide is evolved. The former compound is an oily liquid with boiling point 230° C., while the latter forms colorless needle-shaped crystals melting at 88–89° C.

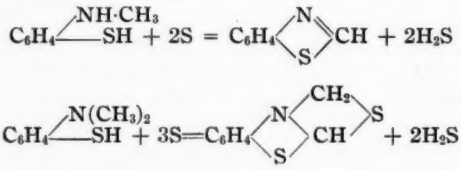
In the reaction products of monomethylaniline and sulfur, one can find the same compounds in the melt, though there will be some differences between their yields compared with the yields in the former case.

The formation of the same products can be explained by thermal decomposition of two molecules of monomethylaniline into one molecule of aniline and dimethylaniline, which reacts with sulfur on being heated. In the case of a dimethylaniline-sulfur melt, however, a part of the dimethylaniline will decompose to produce monomethylaniline as shown in the equation:

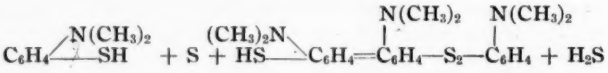
$$C_6H_5{\cdot}N(CH_3)_2 + 3S \longrightarrow C_6H_5{\cdot}NH{\cdot}CH_3 + CS_2 + H_2S$$

This is the reason why the same product can be found in both cases. Now, methylaminophenylmercaptan is the direct reaction product of monomethylaniline and sulfur, whereas benzothiazolemethenesulfide seems to be the direct product of dimethylaniline; because in both cases the formation of aminothiophenol is as-

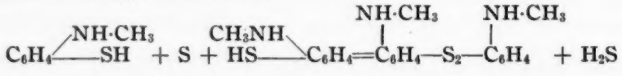
sumed as an intermediate product. The production of these two compounds can be easily explained as follows:



But in the dimethylaniline-S melt, the writer isolated a small quantity of another compound, yellow needle-shaped crystals, melting at 118° C. As the result of elementary analysis and in view of its melting point, this compound was tetramethyldiaminophenyldisulfide, which can be easily produced by the action of sulfur monochloride on dimethylaniline by applying the method of Merz and Weith (*Ber.*, 19 (1886), 1571). Now mixing the crystals isolated from the dimethylaniline-S melt with tetramethyldiaminophenyldisulfide the rise or fall of the melting point was measured, but no variation in the melting point was noticed; which confirms the view that these two compounds are the same. The formation of tetramethyldiaminophenyldisulfide can be explained as follows, assuming the formation of thiophenol in the intermediate stage of reaction:



Similarly the formation of dimethyldiaminophenyldisulfide from monomethylaniline seems to be quite probable by the following equation, though the isolation of the crystals cannot yet be effected:



Summarizing the above conclusions, it can be stated that the direct sulfur products of monomethylaniline are dimethyldiaminophenyldisulfide and methylaminophenylmercaptan, but the direct products of dimethylaniline and sulfur are tetramethyldiaminophenyldisulfide and benzothiazolemethenesulfide.

The production of the disulfides in the melts is very small in quantity compared with that in the case of aniline, owing probably to the weaker basic property of the two compounds than that of aniline.

As in the former experiments, the effects of these four sulfides on vulcanization are examined with rubber compounds having the following composition:

No. of sample	Composition			Chemical names
	Rubber	Sulfur	Sulfide	
1	92.5	7.5	1.48	Dimethyldiaminophenyldisulfide
2	92.5	7.5	1.45	Methylaminophenylmercaptan
3	92.5	7.5	1.64	Tetramethyldiaminophenyldisulfide
4	92.5	7.5	1.94	Benzothiazolemethenesulfide

The quantities of sulfides used for 100 parts of rubber-S compound are the equimolecular quantity corresponding to 1.15 parts of monomethylaniline and 1.31 parts of dimethylaniline, respectively, and dimethyldiaminophenyldisulfide used for the compounding is made by the method of Harries and Lowenstein (*Ber.*, 27 (1897), 863).

All the conditions for vulcanizing the compounds are quite the same as in the former cases.

TABLE 9

EFFECT ON VULCANIZATION OF THE DISULFIDES DERIVED FROM MONOMETHYLANILINE

No. 1 (A) When sample No. 1 was heated in air (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	10.04	0.67	0.75	0.75	0
30	9.69	0.98	1.10	0.98	+0.12
45	9.12	1.47	1.64	1.32	+0.32
60	8.87	1.98	2.22	1.72	+0.50

(B) When sample No. 1 was heated in CO_2 gas (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	10.00	0.69	0.77	0.79	−0.02
30	9.63	1.07	1.20	1.15	+0.05
45	8.99	1.57	1.76	1.64	+0.12
60	8.74	2.12	2.38	2.10	+0.28

(C) When sample No. 1 was heated in H_2S (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	9.80	1.08	1.21	0.87	+0.34
30	9.30	1.73	1.94	1.25	+0.69
45	8.71	2.28	2.56	1.80	+0.76
60	7.54	3.57	4.02	2.48	+1.54

No. 2 (A) When sample No. 2 was heated in air (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	10.29	0.42	0.47	0.75	−0.28
30	9.68	0.72	0.80	0.98	−0.18
45	9.22	0.80	0.89	1.32	−0.43
60	8.89	1.11	1.24	1.72	−0.48

(B) When sample No. 2 was heated in CO_2 gas (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	10.15	0.52	0.58	0.79	−0.21
30	9.79	0.74	0.83	1.15	−0.32
45	9.04	1.15	1.28	1.64	−0.36
60	8.34	1.47	1.63	2.10	−0.47

(C) When sample No. 2 was heated in H_2S (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	9.91	0.55	0.61	0.87	−0.26
30	8.61	1.05	1.16	1.25	−0.09
45	8.25	1.59	1.76	1.80	−0.04
60	7.86	2.00	2.22	2.48	−0.26

TABLE 10

EFFECT ON VULCANIZATION OF THE SULFIDES DERIVED FROM DIMETHYLANILINE

No. 1 (A) When sample No. 3 was heated in air (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	10.80	0.84	0.95	0.75	+0.20
30	9.98	1.44	1.62	0.98	+0.64
45	9.23	2.05	2.31	1.32	+0.99
60	8.52	2.88	3.25	1.72	+1.53

(B) When sample No. 3 was heated in CO_2 gas (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	10.70	0.83	0.94	0.79	+0.15
30	9.84	1.39	1.57	1.15	+0.42
45	8.72	2.30	2.58	1.64	+0.94
60	8.18	3.13	3.53	2.10	+1.43

(C) When sample No. 3 was heated in H_2S (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	10.22	1.66	1.88	0.87	+1.01
30	9.22	2.93	3.34	1.25	+2.09
45	7.75	4.33	4.93	1.80	+3.13
60	7.08	5.39	6.16	2.48	+3.68

No. 2 (A) When sample No. 4 was heated in air (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	11.57	0.61	0.69	0.75	−0.06
30	11.00	0.80	0.90	0.98	−0.08
45	10.67	0.95	1.08	1.32	−0.24
60	10.31	1.21	1.3	1.72	−0.36

(B) When sample No. 4 was heated in CO_2 (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	11.04	0.63	0.71	0.79	−0.08
30	10.92	0.85	0.96	1.15	−0.19
45	10.50	1.21	1.37	1.64	−0.27
60	10.00	1.53	1.73	2.10	−0.37

(C) When sample No. 4 was heated in H_2S (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	11.00	0.63	0.71	0.87	−0.16
30	10.75	1.22	1.39	1.25	+0.14
45	10.30	1.70	1.93	1.80	+0.13
60	9.71	2.18	2.47	2.48	−0.01

As shown in the foregoing tables, the real active principles of accelerators found in the sulfur melts are dimethyldiaminophenyldisulfide and tetramethyldiaminophenyldisulfide. These disulfides react as strong accelerators in association with hydrogen sulfide. On the other hand, these disulfides are easily reducible by H_2S to their corresponding "thiophenols," which, if heated with sulfur, oxidize again to their disulfides.

Inasmuch as these relations are quite similar to those of the disulfide produced from aniline, the reaction mechanism proposed for aniline in the last chapter is likewise applicable to its homologs.

But owing to the difficulties involved in the formation of the polysulfides due to their weak basic nature, the action of monomethylaniline and of dimethylaniline as accelerators is greatly limited.

Moreover, methylaminophenylmercaptan and benzothiazolemethenesulfide have no positive power at all to accelerate any vulcanization. On the contrary when heated in an oxidizing or inert gas these compounds react as negative accelerators.

Judging from the excess-S coefficient in Table 10 (A) and (B) of Sample No. 3, the disulfide from dimethylaniline seems to be effective as an accelerator even when it is used without H_2S.

But the feel of the cured stocks by thumb test is somewhat sticky, showing that they are still in the state of "undercure," this being especially noticeable in the case of (A).

These effects can be seen in the tensile strength of the cured compounds, which will be given later.

On the Reactions of *p*-Toluidine as an Accelerator

p-Toluidine is one of the notable compounds among the accelerators of the aniline series. It has the strongest action among the three modifications of toluidine (α, β, γ).

Parallel with the former experiments may be placed those of the rubber compounds with the following composition—92.5 parts rubber, 7.5 parts S, and 1.15 parts *p*-toluidine—which were heated in the vulcanizing apparatus at 145° C.

The results obtained were as follows:

Table 11

Effect of *p*-Toluidine as an Accelerator

(A) When the compounds were heated in air (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	9.87	0.96	1.08	0.75	+0.33
30	9.29	1.59	1.78	0.98	+0.80
45	8.60	2.14	2.40	1.32	+1.08
60	7.64	2.80	3.13	1.72	+1.41

(B) When the compounds were heated in CO_2 (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	9.90	0.97	1.09	9.79	+0.30
30	8.71	1.85	2.07	1.15	+0.92
45	7.84	2.58	2.88	1.64	+1.24
60	7.10	3.24	3.62	2.10	+1.52

(C) When the compounds were heated in H_2S (Temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	9.61	1.17	1.31	0.87	+0.44
30	8.68	2.13	2.39	1.25	+1.14
45	7.84	2.73	3.05	1.80	+1.25
60	6.89	3.69	4.13	2.48	+1.65

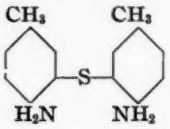
From the above results it is evident that when compared in equimolecular quan-

tity, the action of *p*-toluidine on vulcanization is more marked than that of aniline, monomethylaniline or dimethylaniline.

The Reaction Product of *p*-Toluidine and Sulfur

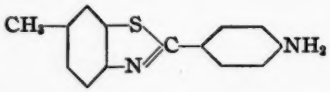
When *p*-toluidine and sulfur are heated together, various products are formed, depending upon the proportions of the initial materials, temperature and duration of heating, presence or absence of hydrogen sulfide absorbents, such as litharge, and other factors.

Among these products, the first compound isolated by Merz and Weith (*Ber.*, 4 (1871), 392–393) from the melt obtained by heating *p*-toluidine and sulfur at 140° C. in the presence of litharge was "thio-*p*-toluidine," a colorless slab-like crystal with m. p. 103–104° C., whose constitution was afterwards determined as bis(amino-2-methyl-5-phenyl)monosulfide.



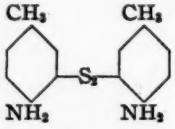
$(C_{14}H_{16}N_2S)$

Another compound isolated from the reaction product of *p*-toluidine and sulfur is "dehydrothioparatoluidine," which occurs in the melt heated at 170–180° C. in the presence of naphthalene as a catalyst. The constitution of this compound is as follows:



When heated further with more sulfur, this compound produces the so-called "primulin base," an important product for dyestuff-making.

Recent study on this subject made by Bogert and Mandelbaum (*J. Amer. Chem. Soc.*, 45 (1923), 3045) adds a new sulfide, "dithioparatoluidine," produced in the *p*-toluidine-S melt at 140° C. with hydrogen sulfide absorbent. This new sulfide forms green, needle-shaped crystals with m. p. 88.5–89° C., the constitution of which is as follows:



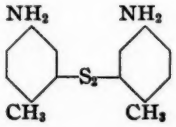
The writer examined the melt which is obtained by heating *p*-toluidine and sulfur in proportion of 500 parts to 230 parts, at a temperature of 160° C., for a long time. As the main product, dithio-*p*-toluidine was produced, accompanied by a small amount of thio-*p*-toluidine. But in the presence of litharge as the absorbent of hydrogen sulfide, the main product in the melt was thio-*p*-toluidine.

This relation is similar to that of aniline-S melt. Besides these two sulfides which are already found in the melt, the generation of bis(methyl-2-amino-5-phenyl)disulfide seems to be probable as an isomer of dithio-*p*-toluidine, though the amount produced will be too trifling to be isolated as crystals. An analogous example can be seen in the melt of aniline and sulfur, in which *p*-diaminophenyldisulfide is separated as an isomer of the orthodisulfide compound as already mentioned.

This compound forms yellow needle-shaped crystals with m. p. 94° C., which

can be produced by the method of Zinke and Rohlhauser (*Ber.*, 45 (1912), 1496–1501).

The formula is as follows:



An equimolecular quantity of these four sulfides is mixed with each of the control mixtures, and the effects of the sulfides on vulcanization were examined under the same condition and in a similar manner to the previous experiments.

The compositions of the rubber compounds used for the test were as follow:

No. of sample	Rubber	Sulfur	Sulfide	Chemical names
1	92.5	7.5	1.48	(Bis(methyl-5-phenyl amino 2-)disulfide)
2	92.5	7.5	1.48	(Bis(methyl-2-amino-5-phenyl)disulfide)
3	92.5	7.5	1.31	(Bis(methyl-5-amino-2-phenyl)monosulfide)
4	92.5	7.5	1.29	(Dihydrothio-*p*-toluidine)

TABLE 12

THE EFFECTS ON VULCANIZATION OF THE SULFIDES, WHICH ARE PRODUCED IN *p*-TOLUIDINE-SULFUR MELT

No. 1 (A) When sample No. 1 is heated in air (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	9.84	0.86	0.96	0.75	+0.21
30	9.70	1.21	1.36	0.98	+0.38
45	9.30	1.68	1.89	1.32	+0.57
60	8.68	2.26	2.54	1.72	+0.82

(B) When sample No. 1 is heated in CO_2 (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	9.70	0.90	1.01	0.79	+0.22
30	9.40	1.39	1.56	1.15	+0.41
45	9.00	1.95	2.20	1.64	+0.56
60	8.33	2.55	2.87	2.10	+0.77

(C) When sample No. 1 is heated in H_2S (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	9.73	1.07	1.20	0.87	+0.33
30	9.04	2.19	2.47	1.25	+1.22
45	8.18	3.22	3.64	1.80	+1.84
60	6.89	4.62	5.22	2.48	+2.74

No. 2 (A) When sample No. 2 is heated in air (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	10.22	0.99	1.11	0.75	+0.36
30	8.89	2.06	2.31	0.98	+1.33
45	7.68	3.07	3.44	1.32	+2.12
60	6.48	4.12	4.61	1.72	+2.89

(B) When sample No. 2 is heated in CO_2 (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	10.41	0.91	1.03	0.79	+0.24
30	8.64	2.17	2.43	1.15	+1.28
45	7.21	3.35	3.75	1.64	+2.11
60	6.59	4.14	4.64	2.10	+2.54

(C) When sample No. 2 is heated in H_2S (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	9.69	1.51	1.70	0.87	+0.83
30	8.33	2.97	3.35	1.25	+2.10
45	6.92	4.51	5.09	1.80	+3.29
60	5.60	5.51	6.19	2.48	+3.71

No. 3 (A) When sample No. 3 is heated in air (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix	Excess S coef.
15	10.31	0.71	0.80	0.75	+0.05
30	10.27	1.24	1.40	0.98	+0.42
45	9.72	1.68	1.90	1.32	+0.58
60	9.24	2.25	2.54	1.72	+0.82

(B) When sample No. 3 is heated in CO_2 (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	10.23	0.70	0.78	0.79	−0.01
30	9.80	1.33	1.50	1.15	+0.35
45	9.32	1.88	2.12	1.64	+0.48
60	8.46	2.69	3.03	2.10	+0.93

(C) When sample No. 3 is heated in H_2S (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	10.34	0.85	0.96	0.87	+0.09
30	9.84	1.68	1.90	1.25	+0.65
45	9.19	2.49	2.81	1.80	+1.01
60	8.52	3.29	3.73	2.48	+1.25

No. 4 (A) When sample No. 4 is heated in air (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	10.80	0.83	0.94	0.75	+0.19
30	10.46	1.23	1.39	0.98	+0.41
45	9.93	1.67	1.89	1.32	+0.57
60	8.72	2.06	2.31	1.72	+0.59

(B) When sample No. 4 is heated in CO_2 (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	10.66	0.94	1.06	0.79	+0.27
30	10.07	1.52	1.72	1.15	+0.57
45	9.69	2.07	2.35	1.64	+0.71
60	9.02	2.55	2.88	2.10	+0.78

(C) When sample No. 4 is heated in H_2S (temp., 145° C.)

Time of heating, min.	Acetone extract, %	Combined sulfur, %	Coef. of vul.	C. V. control mix.	Excess S coef.
15	10.59	1.10	1.24	0.87	+0.37
30	9.89	1.61	1.82	1.25	+0.57
45	9.37	2.18	2.47	1.80	+0.67
60	8.65	2.92	3.30	2.48	+0.82

These results serve to show that bis(methyl-5-amino-2-phenyl)disulfide, which is compounded in sample No. 1, reacts as a strong accelerator only when it is heated in hydrogen sulfide, whereas its action in other cases (A) or (B) is very trifling. While another disulfide compounded in sample No. 2 reacts as a strong accelerator in all cases, its action in hydrogen sulfide is still more remarkable. Both of these disulfides in samples No. 1 and No. 2 are reducible by hydrogen sulfide to their corresponding aminothiophenol, which can be oxidized again to disulfide by sulfur or oxygen.

Now, the principal product isolated from the melt of *p*-toluidine and sulfur is the disulfide in sample No. 1; and that in No. 2 is only a by-product produced in small quantity and is associated with the former.

The relation of these two disulfides in their occurrence and their behavior to each other is very similar in every respect to that of ortho- and paradiaminophenyldisulfide which are produced from aniline and sulfur.

Bis(methyl-5-amino-2-phenyl)monosulfide and dihydrothio-*p*-toluidine, which are compounded in samples No. 3 and No. 4, have some action on vulcanization, though their effects are less than those of the disulfides. Moreover, in the actual condition in which the process of vulcanization is carried on, the formation of these compounds in the melt seems to be nil or almost negligibly small.

In view of these facts, we may consider the real active principles of *p*-toluidine during vulcanization are bis(methyl-5-amino-2-phenyl)disulfide and hydrogen sulfide or (methyl-5-amino-2-)thiophenol as their reduction product.

As for the other sulfides, their effects on vulcanization are only of a subsidiary nature, because though they might be produced in the melt their quantities are too trifling to be considered as essential.

Thus the reaction mechanism proposed for aniline as an accelerator can also be applied to the case of *p*-toluidine.

Another similarity noticed between aniline and *p*-toluidine is the behavior of their monosulfides. These compounds do not increase their accelerating power in the presence of hydrogen sulfide as greatly as do their corresponding disulfides.

Summary

On the basis of the investigation, the writer reached the following general conclusions on the reactions of aniline and its homologs as accelerators of vulcanization:

(1) When accelerators of aniline series are heated with sulfur at the vulcanizing temperature of ordinary rubber compounds, disulfides and hydrogen sulfide are produced.

(2) These disulfides react as strong accelerators of vulcanization in association with hydrogen sulfide.

(3) The disulfides can be reduced by hydrogen sulfide to their corresponding aminothiophenols and free sulfur, while the thiophenols can be oxidized again to the disulfides by the action of sulfur. In this oxidizing process, the temporary formation of unstable polysulfides, which may be decomposed to disulfide and active sulfur by heat, seems to be very probable.

(4) These reactions are common to aniline and its allied compounds, such as

monomethylaniline, dimethylaniline and *p*-toluidine. So the hypothesis proposed for the reaction of aniline as an accelerator may also be applied to its kindred compounds.

(5) The action of aniline and its homologs as accelerators is influenced to a certain degree by the properties of the disulfides produced. Still for the most part it depends on the quantity of polysulfide or disulfide produced, which may be chiefly controlled by the basic nature of the accelerators. Among the accelerators above mentioned, the more basic the compound is, the more actively does it react on rubber during vulcanization.

(6) Besides the essential products, some small quantities of sulfides may be produced in the melt, which are the isomers of the disulfide and monosulfide or something else.

These sulfides react generally to assist the reaction of the disulfides as the accelerators, but a few compounds, such as methylaminophenylmercaptans from monomethylaniline and benzothiazolemethenesulfide from dimethylaniline, sometimes react as negative accelerators.

(7) Among the by-products above referred to, some compounds such as *p*-diaminophenyldisulfide and bis(methyl-2-amino-5-phenyl)disulfide have a strong action as accelerators when used in the ordinary way.

These compounds may be found useful as new accelerators in practical work.

Thermal Changes during Vulcanization

In the preceding sections, the principal research is limited to the chemical changes of aniline and its homologs during the vulcanization of rubber.

The vulcanizing phenomenon, like any other chemical change in general, is responsive to thermal change, and, therefore, the thermal change of rubber compounds is a very important factor to be noticed, because the velocity of vulcanization is greatly influenced by it.

References on this subject are found in the studies of Weber, as the pioneering work (Weber, "The Chemistry of India Rubber," 1902, p. 114), and the work of Seidle (Seidle, *Gummi-Ztg.*, 25 (1911), 710, 798). In these studies, the fundamental cause of the thermal changes during vulcanization was left untouched.

Recently a research on this subject has been published by Williams and Beaver (*J. Ind. and Eng. Chem.* 15 (1923), 255).

Their investigations were chiefly carried out on the thermal changes caused during vulcanization by some organic accelerators, i. e., hexamethylenetetramine and piperidylthiuramdisulfide, etc. The results of the research are as follows:

When rubber is heated with sulfur there is (1) at first an evolution of a small amount of heat; (2) a slight absorption of heat which becomes noticeable towards the end of the reaction; (3) a liberation of heat due to a rubber-sulfur reaction because there is no measurable heat liberated in the reaction between rubber-accelerator, sulfur-resin, or sulfur-accelerator; and (4) an increase of reaction caused by the accelerators with increase in percentage of sulfur, or increase in temperature. (3) and (4) are very important in the case of the writer's consideration, but owing to the difference of the accelerators used in the two cases, a repetition of the experiments using the compounds of the aniline series seemed necessary.

So the thermal changes caused by the reaction of sulfur-resin, rubber-accelerator and of accelerator-sulfur were examined by the same method used by Williams and Beaver.

The result of this examination showed that (1) there is no measurable heat evolved in the reaction between rubber-accelerator or sulfur-accelerator when the mixtures are heated at 175° C., (2) there was a slight heat evolution in the reaction

between resin and sulfur, as shown by Williams, but the rise of the temperature in the melt above the heating medium was only about one degree Celsius.

Next the temperature changes of the rubber compounds during vulcanization were examined with the following samples, the composition of which is seen in Table 13.

TABLE 13

COMPOSITION OF THE "RUBBER COMPOUNDS"

No. of sample	Rubber	Sulfur	Accelerator	Name of accelerator
1	92.5	7.5	0	
2	92.5	7.5	1.0	Aniline
3	92.5	7.5	1.15	Monomethylaniline
4	92.5	7.5	1.31	Dimethylaniline
5	92.5	7.5	1.15	*p*-Toluidine
6	92.5	7.5	1.34	*o*-Diaminophenyldisulfide
7	92.5	7.5	1.34	*p*-Diaminophenyldisulfide
8	92.5	7.5	1.16	*o*-Diaminophenylmonosulfide
9	92.5	7.5	1.48	Dimethyldiaminophenyldisulfide
10	92.5	7.5	1.64	Tetramethyldiaminophenyldisulfide
11	92.5	7.5	1.48	Bis(methyl-5-amino-2-phenyl)disulfide
12	92.5	7.5	1.48	Bis(methyl-2-amino-5-phenyl)disulfide
13	92.5	7.5	1.31	Bis(methyl-5-amino-2-phenyl)monosulfide

Apparatus and Procedure

The apparatus and the procedure chosen for measuring the temperature-change during vulcanization were similar to those used by Williams and Beaver.

The temperature change was recorded as indicated at the center of a uniform cylinder made of the sample when the cylinder was immersed in a constant-temperature bath. The rubber compound was calendered to a thin sheet, which was cut into strips of about 10 cm. wide. A thin-walled glass capillary was then placed with the closed end at the center of the strip of rubber, and the strip was rolled about the capillary until a cylinder of the desired size was obtained.

This was then slipped into a close-fitting hard glass tube 1.4 cm. in diameter, and sealed in place with a cork through which the glass capillary projected.

A special device was used to prevent the slipping of the capillary end from the center of the cylinder.

The temperature at the center of the cylinder was measured by means of a silver-constantan thermocouple, which was placed in the glass capillary. The electromotive force produced was measured by a millivoltmeter and thus the writer was able to record temperature changes to 0.5° C.

Heating was done in an oil-bath of about 3-liter capacity, the temperature of which could be kept constant with fluctuations not exceeding 0.5° C. during the vulcanizing process. To maintain the constant temperature of the heating medium, 2 kinds of Bunsen burners were used, the main one being a large-sized burner connected with a pressure governor, and the auxiliary one, a small burner with screw adjustment for regulating the supply of gas.

A series of tests of the temperature changes were made with 13 rubber compounds with varying temperatures of the oil-bath, 145° C., 155° C., 165° C., and 175° C.

Besides the ordinary way of temperature measurements, a special method was applied to 8 samples (No. 6–No. 13) to find out the temperature change of rubber compound, which is associated with hydrogen sulfide. For this purpose, the rubber compounds, which were previously saturated with hydrogen sulfide, were introduced into special test tubes, provided with a capillary tube at the end by which

hydrogen sulfide could be supplied during the heating. The results are distinguished from the ordinary one (which has suffix "a") by adding suffix "b" to the number of the sample.

The result of these temperature measurements is shown in Table 14. [NOTE: While heating at 145° C., 155° C., the maximum temperatures at the center of the rubber compounds did not rise beyond the temperature of the outer heating medium; and the temperature changes of different samples during the heating were nearly identical with one another, so that the temperature records of many samples except No. 1 were entirely omitted on (1) and (2) in Table 14. But when heated at 165° C. or above, all the samples began to show their own peculiarities of temperature change, and the maximum temperature of each compound rose above the temperature of the oil-bath. This phenomenon was particularly noticeable in heating at 175° C.]

[(*) This mark in the following table is the symbol given to indicate the maximum temperature and the time which was first attained during the heating.]

TABLE 14

TEMPERATURE CHANGE OF THE RUBBER COMPOUNDS DURING VULCANIZATION

(1) Temperature change of the rubber compound on heating at 145° C.

Time of heating in min.	4	6	8	10	12	14	16	18	20	22
	24	26	28	30	32	34				
Temp. change of No. 1 (control mix)	108.5	128.0	138.0	141.5	143.5	144.0	144.5	144.5	*145.0	145.0
	145.0	128.0	138.0	141.5	143.5	144.0				

(2) Temperature change of the rubber compound on heating at 155° C.

Time of heating in min.	4	6	8	10	12	14	16	18	20	22
	24	26	28	30	32	34				
Temp. change of No. 1 (control mix)	114.0	136.5	147.5	152.5	154.5	154.5	154.5	*155.0	155.0	
	155.0	136.5	147.5	152.5	154.5	154.5				

From the data in Table 14 it is manifest that the maximum temperature of the samples heated at 145° C. and 155° C. did not rise above the temperature of the outer heating medium or oil-bath. This indicates that the progress of vulcanization is so slow that the heat evolved in the rubber-sulfur reaction is lost or counterbalanced by conduction or radiation, and is incapable of raising the temperature of the rubber stock.

But when heated at 165° C. the emission of heat becomes so violent for a while that the temperature of the rubber compound is raised above that of the oil-bath, which phenomenon becomes very distinct on heating at 175° C.

Now it is obvious that the results (3) and (4) given by Williams and Beaver are also true in the case of vulcanization with aniline and its homologs used as accelerators. So the progress of cure by aniline seems to be caused by the reaction of sulfur and accelerator, furnishing to the rubber the active sulfur from their polysulfide. Then the evolution of heat will occur as a result of combination, sulfur and rubber. This heat may sometimes be helpful to a certain extent for the furtherance of vulcanization, and yet it is not the original cause of the progress of vulcanization, but rather the result.

Two important facts are apparent in the data above mentioned. (1) The coefficient of vulcanization in former sections, measured by analysis of the rubber compound cured at a temperature of 145° C., did not suffer measurable variation

(3) Temperature change of rubber compounds on the heating at 165° C.

Time of heating		4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34
No. 1	(Temp. change)	117.5	140.0	159.0	162.5	164.5	165.5	*166.5	166.5	166.5	166.0	166.0	166.0	165.5	165.5	165.5	165.0
No. 2	(Temp. change)	119.0	146.0	156.5	162.0	164.5	166.0	167.0	*167.5	167.5	167.0	167.0	166.5	166.5	166.0	165.5	165.0
No. 3	(Temp. change)	119.0	145.5	157.0	162.0	164.5	165.0	165.5	*166.0	166.0	165.5	165.5	165.5	165.5	165.0	165.0	165.0
No. 4	(Temp. change)	119.5	148.5	159.0	162.0	163.5	164.5	165.5	*167.0	166.5	166.5	166.0	166.0	165.5	165.5	165.5	165.0
No. 5	(Temp. change)	119.5	146.5	159.0	164.5	169.5	169.5	*170.5	169.5	169.0	168.0	167.5	167.0	166.0	165.0	165.0	164.5
No. 6(a)	(Temp. change)	117.5	145.0	158.0	162.0	163.0	164.0	165.0	*166.5	166.0	166.0	165.5	165.5	165.5	165.0	165.0	164.5
No. 6(b)	(Temp. change)	116.5	141.5	154.5	162.0	164.5	166.5	*168.5	167.5	166.5	166.0	166.0	165.5	165.5	165.0	165.0	165.0
No. 7(a)	(Temp. change)	116.0	140.0	154.5	160.5	165.0	167.0	168.5	*169.5	168.5	168.0	167.0	167.0	166.0	165.5	165.5	165.0
No. 7(b)	(Temp. change)	116.5	142.5	155.5	162.5	165.5	168.0	*170.0	170.0	169.0	168.0	167.0	167.0	166.0	166.0	165.5	165.0
No. 8(a)	(Temp. change)	116.0	140.0	156.5	161.5	163.5	165.0	166.0	*166.5	166.0	166.0	165.5	165.5	165.0	165.0	165.0	164.5
No. 8(b)	(Temp. change)	116.0	139.0	156.0	161.0	164.0	165.0	167.0	*167.5	167.0	166.5	166.5	166.0	165.5	165.0	165.0	165.0
No. 9(a)	(Temp. change)	118.0	144.5	159.0	161.5	163.5	165.0	166.0	*166.5	166.5	166.0	166.0	166.0	165.5	165.5	165.5	165.0
No. 9(b)	(Temp. change)	119.5	150.0	160.0	162.0	164.0	166.0	166.5	*167.5	167.0	167.0	166.5	166.5	166.0	165.5	165.5	165.0
No. 10(a)	(Temp. change)	117.0	148.0	158.0	163.0	165.0	166.0	166.0	*166.5	166.5	166.5	166.0	166.0	165.5	165.5	165.0	165.0
No. 10(b)	(Temp. change)	116.0	143.5	156.0	161.5	163.5	165.0	167.0	*167.5	167.5	166.5	166.0	166.0	166.0	165.5	165.0	165.0
No. 11(a)	(Temp. change)	116.0	145.0	157.0	160.5	163.5	165.0	165.5	*166.0	166.0	165.5	165.5	165.5	165.0	165.0	165.0	165.0
No. 11(b)	(Temp. change)	116.5	142.5	156.0	160.5	164.5	165.0	166.0	*167.0	166.5	166.0	166.0	165.5	165.5	165.5	165.0	165.0
No. 12(a)	(Temp. change)	120.0	151.0	161.5	164.0	165.0	166.0	*167.5	166.5	166.5	166.0	166.0	165.5	165.5	165.0	165.0	165.0
No. 12(b)	(Temp. change)	119.5	151.0	161.0	163.5	165.0	165.5	166.0	*167.5	166.5	166.5	166.0	166.0	165.5	165.5	165.0	165.0
No. 13(a)	(Temp. change)	116.0	141.0	158.0	161.5	164.5	165.5	166.0	*166.5	166.5	166.5	166.0	166.0	166.0	165.5	165.5	165.0
No. 13(b)	(Temp. change)	116.5	143.5	157.5	160.5	163.5	164.5	166.0	*167.0	166.5	166.5	166.0	166.0	165.5	165.5	165.0	165.0

(4) Temperature change of rubber compounds on heating at 175° C.

No. 1	(Temp. change)	122.5	152.0	168.0	173.5	176.0	178.0	*180.5	180.0	179.0	178.0	177.0	176.5	176.0	175.5	175.5	175.0
No. 2	(Temp. change)	123.0	148.0	161.5	170.0	176.0	179.5	182.0	*182.5	180.0	178.0	176.5	175.5	175.0	174.5	174.5	174.5
No. 3	(Temp. change)	124.5	150.0	164.5	171.5	175.0	177.5	179.5	*180.5	180.0	179.5	178.0	177.0	176.5	175.5	175.5	175.0
No. 4	(Temp. change)	124.5	155.5	168.0	172.5	176.0	178.5	180.0	*182.0	181.5	180.0	179.5	178.5	177.0	176.5	175.5	175.0
No. 5	(Temp. change)	123.5	149.5	164.0	172.5	179.5	183.0	*183.5	181.5	179.0	178.0	177.0	176.0	175.5	175.0	174.5	174.5
No. 6(a)	(Temp. change)	119.5	151.5	167.5	174.0	178.0	180.0	*181.0	180.0	179.0	177.5	176.5	175.5	175.5	175.0	175.0	174.5
No. 6(b)	(Temp. change)	119.5	152.5	167.0	174.0	178.0	182.0	*183.5	182.0	180.0	178.0	177.0	176.0	175.5	175.5	175.0	175.0
No. 7(a)	(Temp. change)	124.0	153.0	167.5	176.0	180.5	*182.0	181.5	178.0	176.5	176.5	175.5	175.5	175.0	175.0	174.5	174.5
No. 7(b)	(Temp. change)	123.5	152.5	167.0	176.0	181.0	*184.5	182.5	180.0	177.0	176.0	176.0	175.5	175.0	175.0	174.5	174.5
No. 8(a)	(Temp. change)	119.0	147.0	163.0	173.0	177.0	179.0	*180.5	179.0	177.0	176.0	175.5	175.5	175.0	175.0	175.0	175.0
No. 8(b)	(Temp. change)	124.0	150.0	166.5	173.0	178.0	180.0	*181.0	178.5	176.5	175.5	175.5	175.0	175.0	174.5	174.5	174.5
No. 9(a)	(Temp. change)	119.5	152.5	167.0	173.5	178.0	180.0	*180.5	179.0	177.5	176.0	175.5	175.5	175.0	175.0	174.5	174.5
No. 9(b)	(Temp. change)	123.5	154.5	169.5	175.0	179.0	180.5	*181.5	179.5	178.0	177.0	176.5	176.0	176.0	175.5	175.0	175.0
No. 10(a)	(Temp. change)	120.0	155.0	170.0	175.0	179.5	180.5	*181.5	180.0	179.0	177.5	177.0	176.5	175.5	175.5	175.0	175.0
No. 10(b)	(Temp. change)	119.5	149.5	166.5	173.5	178.5	181.5	*182.5	181.5	178.5	176.5	176.0	175.5	175.5	175.0	175.0	174.5
No. 11(a)	(Temp. change)	120.0	152.5	166.5	173.5	178.0	180.5	*181.0	180.5	179.0	177.5	176.5	176.0	176.0	175.5	175.5	175.0
No. 11(b)	(Temp. change)	119.5	148.0	166.5	173.5	177.0	181.5	*183.0	181.5	179.5	177.5	176.5	176.0	175.5	175.5	175.0	175.0
No. 12(a)	(Temp. change)	122.5	152.5	167.0	175.5	180.5	*183.0	180.5	178.5	177.0	175.5	175.0	175.0	174.5	174.5	174.5	174.5
No. 12(b)	(Temp. change)	123.5	153.5	167.5	174.5	179.0	*184.0	183.0	179.5	179.0	177.5	176.0	175.5	175.5	175.0	175.0	174.5
No. 13(a)	(Temp. change)	121.5	149.5	166.5	172.0	175.5	178.0	179.0	*180.0	178.5	177.0	176.0	175.5	175.5	175.0	175.0	175.0
No. 13(b)	(Temp. change)	122.0	153.0	166.5	171.5	175.5	178.5	*180.5	179.0	177.5	177.0	176.5	176.0	175.5	175.5	175.0	175.0

by heat due to rubber-sulfur reaction, because the temperature of the compounds did not rise above the heating medium during vulcanization. This fact denotes that the action of the accelerator in that case is chiefly chemical, and not thermal.

(2) The stronger the accelerator which is added to a rubber-sulfur compound, the higher becomes the temperature of the rubber stock during vulcanization.

In the case of (4) in Table 14, for instance, when the maximum temperatures of the samples No. 1 to No. 5 are compared, the highest is No. 5, which is compounded with *p*-toluidine; No. 2 containing aniline comes next, No. 4 with dimethylaniline is the 3rd, and No. 3 with monomethylaniline and No. 1, the control mixture, are at the end. At the same time, if the accelerators are arranged in order of their action according to the excess-sulfur coefficients, the order will coincide with the above (compare the coef. of vulcanization of rubber compound with these accelerators in earlier sections).

This relation is generally maintained to be true among the sulfides produced from aniline and its homologs; so the result (2) above mentioned can be used as a method for testing the relative action of accelerators if one chooses the proper temperature of heating, say, 175° C. or above.

It is also suggested that there may be some relation between the action of the accelerators and lapse of time required in reaching the maximum temperature in the above cases, but this relation is still too uncertain to furnish any definite conclusion.

[NOTE: In (3) and (4) of Table 14, there are great temperature variations between samples of the corresponding columns, i. e., the 3rd or 4th columns from the left. This is not brought about by the internal heat changes, but is caused by a very little difference in thickness of rubber or of glass walls, owing to the very rapid temperature elevation from the outside. Hence the temperature difference is minimized after the lapse of about ten minutes' heating, so that all the samples reach almost a uniform temperature.

The temperature variation thereafter is the result of internal heat evolution, and this temperature deviation is well worthy of notice.

In the determination of the thermal changes the writer used test tubes and capillaries of uniform size and thickness, selected with the utmost care; still some variations could not be entirely eliminated. These results, therefore, cannot be said to be free from errors of this nature, yet all the data above mentioned are reliable enough for the purpose of ascertaining the general tendency of thermal changes.]

Physical Properties of Vulcanized Rubber Compound

Tensile Strength at Break and the Percentage Elongation

In the preceding investigation, the degree of vulcanization of the rubber stock was measured by the percentage of combined sulfur.

But inasmuch as the physical properties of rubber are not merely a function of combined sulfur, the degree of vulcanization is estimated, for technical purposes, by measuring the tensile strength at break and the percentage elongation of the cured stock, as this is considered to be more convenient and practical in most cases. In contrast to the former experiments, the tensile strength and the elongation of the vulcanized rubber compound which was cured under the same condition as in the former case, was measured by means of the same vulcanizing apparatus. During the vulcanization of the compounds, air, nitrogen or hydrogen sulfide was also introduced into the heating chamber.

From the rubber stock, cured as a narrow rectangular slab 1.5–3.0 mm. thick, a bar-shaped test piece was punched out and its tensile strength and elongation are measured by Schopper's testing machine.

The test piece thus prepared was not so smooth in surface as that made by the press cure. Moreover, it was somewhat porous. Consequently, the result of this experiment is somewhat inaccurate and its tensile strength is markedly weaker than that of an ordinary test piece made by the press-vulcanizer.

For the inert gas in the heating chamber, nitrogen gas was used instead of carbon dioxide gas, because when carbon dioxide gas was used the porosity of the cured stock became too great for the physical testing. The compositions of samples are given in Table 13. The heating conditions were exactly the same as those of the former experiments with the oil-bath at the constant temperature of 145° C.

The result of this physical test is given in Table 15.

TABLE 15

TENSILE STRENGTH AT BREAK AND THE PERCENTAGE ELONGATION OF THE VULCANIZED RUBBER STOCK

Sample No. 1 "control mixture"

Time of heating, min.	Samples heated in "air" T. S. at break, kg./sq. cm.	% elong.	in "nitrogen" T. S. at break, kg./sq. cm.	% elong.	in "H_2S" T. S. at break, kg./sq. cm.	% elong.
15	3.2	700	3.1	700	3.0	680
30	9.7	790	12.9	790	12.7	810
45	22.2	840	24.3	820	24.1	840
60	32.7	850	32.8	820	35.0	850
75	36.8	800	44.7	810	58.8	810
90	45.6	770	55.1	770	55.8	740

Sample No. 2 (with aniline)

Time of heating, min.	T. S. at break, kg./sq. cm.	% elong.	T. S., kg./sq. cm.	% elong.	T. S., kg./sq. cm.	% elong.
15	5.8	860	6.9	860	6.4	810
30	18.7	850	23.8	840	28.4	830
45	38.4	820	42.7	845	49.5	860
60	46.9	830	53.8	835	62.3	780
75	56.5	750	57.7	770	65.1	740
90	18.6	460	27.5	490	18.8	330

Sample No. 3 (with monomethylaniline)

Time of heating, min.	T. S. at break, kg./sq. cm.	% of elong.	T. S., kg./sq. cm.	% elong.	T. S., kg./sq. cm.	% elong.
15	1.2	730	2.1	790	3.3	770
30	4.6	850	5.7	850	9.1	860
45	9.5	850	17.4	890	21.1	880
60	22.2	830	22.5	860	36.8	810
75	36.9	780	37.8	810	54.7	790
90	40.2	800	43.9	790	63.0	760

Sample No. 4 (with dimethylaniline)

Time of heating, min.	T. S. at break, kg./sq. cm.	% elong.	T. S., kg./sq. cm.	% elong.	T. S., kg./sq. cm.	% elong.
15	1.2	760	1.5	750	1.5	750
30	5.0	720	5.3	740	6.5	760
45	11.0	840	12.1	810	19.4	870
60	23.9	910	33.1	870	35.8	850
75	37.7	830	40.0	850	57.4	850
90	40.7	750	42.5	780	54.8	760

Sample No. 5 (with *p*-toluidine)

Time of heating, min.	Samples heated in "air"		in "nitrogen"		in "H_2S"	
	T. S. at break, kg./sq. cm.	% elong.	T. S. at break, kg./sq. cm.	% elong.	T. S. at break, kg./sq. cm.	% elong.
15	16.2	900	21.3	930	18.7	930
30	31.4	870	38.2	860	34.0	900
45	49.6	830	56.7	815	55.5	850
60	60.2	790	63.2	790	69.8	760
75	45.3	720	54.6	730	34.9	560
90	15.4	380	14.1	370	14.3	300

Sample No. 6 (with *o*-diaminophenyldisulfide)

Time of heating, min.	T. S. at break, kg./sq. cm.	% elong.	T. S., kg./sq. cm.	% elong.	T. S., kg./sq. cm.	% elong.
15	1.0	730	1.0	700	5.2	750
30	7.7	780	9.2	800	24.7	850
45	22.4	860	24.5	830	48.5	830
60	32.1	845	37.2	840	75.2	730
75	30.6	770	35.2	760	19.9	380
90	25.7	640	23.6	620	15.4	300

Sample No. 7 (with *p*-diaminophenyldisulfide)

Time of heating, min.	T. S. at break, kg./sq. cm.	% elong.	T. S., kg./sq. cm.	% elong.	T. S., kg./sq. cm.	% elong.
15	5.9	720	...	...	6.2	710
30	30.3	900	...	...	45.5	950
45	43.6	810	...	...	85.8	840
60	56.5	830	...	...	49.0	560
75	36.1	680	...	...	23.9	320
90	16.9	410	...	...	17.8	290

Sample No. 8 (with *o*-diaminophenylmonosulfide)

Time of heating, min.	T. S. at break, kg./sq. cm.	% of elong.	T. S., kg./sq. cm.	% of elong.	T. S., kg./sq. cm.	% of elong.
15	4.7	700	..	...	4.4	700
30	13.6	860	..	...	13.1	900
45	21.2	820	..	...	27.5	860
60	41.4	810	..	...	45.1	790
75	44.4	700	..	...	50.0	650
90	37.5	550	..	...	34.2	450

Sample No. 9 (with dimethyldiaminophenyldisulfide)

Time of heating, min.	T. S. at break, kg./sq. cm.	% of elong.	T. S. at break, kg./sq. cm.	% of elong.	T. S. at break, kg./sq. cm.	% of elong.
15	0.5	720	0.5	760	1.0	790
30	4.5	770	4.7	760	10.1	860
45	21.4	910	19.5	910	48.5	910
60	28.1	830	24.7	810	83.5	820
75	31.0	780	33.3	780	31.3	500
90	33.9	740	34.5	700	14.5	340

Sample No. 10 (with tetramethyldiaminophenyldisulfide)

Time of heating, min.	Samples heated in "air" T. S. at break, kg./sq. cm.	% of elong.	in "nitrogen" T. S., kg./sq. cm.	% of elong.	in "H_2S" T. S., kg./sq. cm.	% of elong.
15	0.5	860	0.5	830	1.0	880
30	7.5	860	7.1	820	17.3	830
45	20.9	870	19.5	830	59.7	890
60	27.6	815	30.8	830	113.6	810
75	32.1	780	36.8	780	49.5	760
90	49.7	760	47.8	760	16.2	380

Sample No. 11 (with bis(methyl-5-amino-2-phenyl)disulfide)

Time of heating, min.	T. S. at break, kg./sq. cm.	% of elong.	T. S., kg./sq. cm.	% of elong.	T. S., kg./sq. cm.	% of elong.
15	1.9	800	2.0	790	3.5	780
30	5.5	790	7.2	800	14.4	800
45	17.4	780	20.3	810	38.7	770
60	21.9	810	25.1	820	87.9	880
75	39.1	800	43.7	800	79.9	710
90	40.1	750	45.0	740	18.3	320

Sample No. 12 (with bis(methyl-2-amino-5-phenyl)disulfide)

Time of heating, min.	T. S. at break, kg./sq. cm.	% of elong.	T. S., kg./sq. cm.	% of elong.	T. S., kg./sq. cm.	% of elong.
15	30.4	950	..	...	32.6	920
30	62.4	890	..	...	66.7	890
45	79.5	790	..	...	131.6	810
60	84.2	730	..	...	26.2	430
75	13.3	360	..	...	13.8	280
90	12.9	250	..	...	13.0	200

Sample No. 13 (with bis(methyl-5-amino-2-phenyl)monosulfide)

Time of heating, min.	T. S. at break, kg./sq. cm.	% of elong.	T. S. at break, kg./sq. cm.	% of elong.	T. S. at break, kg./sq. cm.	% of elong.
15	2.5	750	..	...	3.2	850
30	9.9	860	..	...	14.2	890
45	20.5	830	..	...	20.8	825
60	39.6	820	..	...	47.8	870
75	50.4	800	..	...	52.2	780
90	50.2	730	..	...	54.3	670

The result in Table 15 supports the conclusions reached on the reactions of anilines and their sulfides as the accelerator, discussed and demonstrated by chemical analysis in former sections. The significant fact that the disulfides display their actions only when they are associated with hydrogen sulfide is also evident in their physical properties.

Comparison of the Effects of the New and the Well-Known Accelerators on the Physical Properties of Vulcanized Rubber

As already mentioned, the disulfides produced from aniline and its allied compounds by the reaction of sulfur act strongly on vulcanization when they are used in the presence of hydrogen sulfide.

But heating the rubber compound in hydrogen sulfide gas will prove to be too troublesome a method to be applied in industry.

Vulcanizing the rubber compound in a press, which is previously saturated with

H_2S, may be a possible scheme for practical operation. Still there is the inevitable objection to this method that the mould is affected by gas so that the gas is consumed in vain and consequently the action of the sulfide is likely to be weakened.

For these reasons, the disulfides seem to be unsuitable as accelerators for ordinary use; but there are a few disulfides, such as *p*-diaminophenyldisulfide and bis(methyl-2-amino-5-phenyl)disulfide, which remain in force even when they are heated in air in compounds with rubber. Moreover, there are some disulfides of other organic bases which display their efficacy as accelerators, though they are active only when associated with zinc oxide, as Bruni has shown.

Therefore, by compounding the disulfide with rubber as an accelerator either with or without ZnO, the rubber stock is vulcanized in a press in order to ascertain the action of the accelerator on the physical properties of rubber thus vulcanized. To compare the efficacy of accelerators, a parallel test is made using in equal proportion the well-known accelerators such as thiocarbanilide, hexamethylenetetramine and aldehydeammonia.

Thiocarbanilide was known to be an accelerator which is active only when ZnO is added.

Aldehydeammonia can be used effectively without ZnO, while hexamethylenetetramine assumes a position between the two, because it shows some action when it is used without ZnO, though its curing action is greatly increased when compounded with ZnO.

The rubber stock is made by compounding 0.5 part of accelerator to 100 parts of rubber-sulfur compound, to which 10% ZnO is further added as zinc oxide-rubber compound.

Milling conditions are very important for the physical tests. In general, the longer the milling time the weaker is the cured slab in its tensile strength. But as in the writer's experiments it was merely important to ascertain the relative strength; a long period of milling at a low temperature, i. e., 40 min. at 45° C., was adopted in order to get a uniform result.

The press vulcanizer used is a handscrew press, with a working temperature of 145° C. measured at the outlet of the steam pipe which is directly connected with the heating chest.

The ring-shaped test pieces were cut off from the rectangular rubber slab 3 mm. thick vulcanized in a mould under pressure; the sectional area of the ring was about 12 sq. mm.

TABLE 16

THE EFFECTS OF NEW AND WELL-KNOWN ACCELERATORS ON THE PHYSICAL PROPERTIES OF THE CURED RUBBER STOCKS

(1) Control mixture (rubber-sulfur compounds)

Time of heating, min.	Without ZnO		With 10% ZnO	
	T. S. at break, kg./sq. cm.	Elong. (%)	T. S. at break, kg./sq. cm.	Elong. (%)
30	20.8	975	24.7	900
60	45.8	910	54.2	840
90	73.3	870	78.3	805

(2) Rubber-sulfur compound with 0.5% *o*-diaminophenyldisulfide

Time of heating, min.	Without ZnO		With 10% ZnO	
	T. S., kg./sq. cm.	Elong. (%)	T. S., kg./sq. cm.	Elong. (%)
30	12.5	895	29.4	765
60	30.4	910	96.7	745
90	49.2	895	101.5	660

(3) Rubber-S compound with 0.5% *p*-diaminophenyldisulfide

Time of heating, min.	Without ZnO		With 10% ZnO	
	T. S., kg./sq. cm.	Elong. (%)	T. S., kg./sq. cm.	Elong. (%)
30	71.6	905	67.4	810
60	82.5	760	99.0	750
90	100.5	740	112.8	655

(4) R.-S compound with 0.5% dimethyldiaminophenyldisulfide

Time of heating, min.	Without ZnO		With 10% ZnO	
	T. S., kg./sq. cm.	Elong. (%)	T. S., kg./sq. cm.	Elong. (%)
30	20.0	940	25.0	840
60	53.0	910	92.0	815
90	87.0	860	89.0	725

(5) R.-S compound with 0.5% tetramethyldiaminophenyldisulfide

Time of heating, min.	Without ZnO		With 10% ZnO	
	T. S., kg./sq. cm.	Elong. (%)	T. S., kg./sq. cm.	Elong. (%)
30	15.3	830	15.1	735
60	56.0	900	88.0	790
90	87.5	840	100.2	720

(6) R.-S compound with 0.5% bis(methyl-5-amino-2-phenyl)disulfide

Time of heating, min.	Without ZnO		With 10% ZnO	
	T. S. at break, kg./sq. cm.	Elong. (%)	T. S. at break, kg./sq. cm.	Elong. (%)
30	17.2	880	74.1	820
60	53.0	900	143.6	760
90	85.0	840	123.0	660

(7) R.-S compound with 0.5% bis(methyl-2-amino-5-phenyl)disulfide

Time of heating, min.	Without ZnO		With 10% ZnO	
	T. S., kg./sq. cm.	Elong. (%)	T. S., kg./sq. cm.	Elong. (%)
30	107.6	855	110.0	780
60	132.3	765	129.0	710
90	20.0	395	93.2	610

(8) R.-S compound with 0.5% thiocarbanilide

Time of heating, min.	Without ZnO		With 10% ZnO	
	T. S., kg./sq. cm.	Elong. (%)	T. S., kg./sq. cm.	Elong. (%)
30	17.6	965	24.6	845
60	37.4	910	74.3	785
90	64.0	880	94.1	725

(9) R.-S compound with 0.5% hexamethylenetetramine

Time of heating, min.	Without ZnO		With 10% ZnO	
	T. S., kg./sq. cm.	Elong. (%)	T. S., kg./sq. cm.	Elong. (%)
30	37.5	905	113.0	760
60	76.5	895	145.0	615
90	95.5	850	23.0	255

(10) R.-S compound with 0.5% aldehydeammonia

Time of heating, min.	Without ZnO		With 10% ZnO	
	T. S., kg./sq. cm.	Elong. (%)	T. S., kg./sq. cm.	Elong. (%)
30	125.4	820	134.2	750
60	46.1	620	116.6	660
90	24.8	425	64.0	540

As shown in the foregoing tables, the new accelerators, which remarkably increase the tensile strength of rubber when associated with no zinc oxide, are the *p*-diaminophenyldisulfide and the bis(methyl-2-amino-5-phenyl)disulfide, while the other sulfides do not produce any notably good effect on the strength of rubber without ZnO.

As for *o*-diaminophenyldisulfide, it has a tendency rather to decrease the strength of the cured stock.

Now, comparing the effect of two new accelerators above referred to with that of known accelerators used under the same conditions, it is known that the action of bis(methyl-2-amino-5-phenyl)disulfide is slightly inferior to that of aldehydeammonia, but far better than that of hexamethylenetetramine, while that of *p*-diaminophenyldisulfide is a little stronger than that of the latter.

Both of these accelerators are promising in the rubber industry. These results are in accordance with the conclusions made in the preceding work, which are supported by chemical tests.

In cases where the sulfides are compounded in rubber with ZnO, the new accelerators which greatly increase the tensile strength of cured stock are bis(methyl-5-amino-2-phenyl)disulfide and *o*-diaminophenyldisulfide; the former especially has a strong action toward increasing the strength of rubber under the above-mentioned condition. When the effects of these two sulfides are compared according to their respective strength with those of the known accelerators above referred to, the effects of the former are nearly equal to those of hexamethylenetetramine in the ZnO-rubber compound, and those of the latter are similar in their action to those of the thiocarbanilide.

Accordingly, these two sulfides in compounding with ZnO will also find a use as new accelerators.

Speaking from the writer's own experience, these four sulfides which can be used as accelerators with or without ZnO are quite harmless to workmen when they are used as compounding materials in actual work, because they do not cause blisters or rising on the skin. Furthermore the rubber stock compounded with them has no disagreeable odor either before or after vulcanization.

These merits will give them an advantage over most of the accelerators which are in general use today.

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A New Tetramethylbutadiene

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The present investigation was undertaken largely as part of a study of the influence of methyl substitution on the polymerizability of butadiene. The data available on the way in which and the extent to which polymerization is affected by the position and the number of methyl groups which may be introduced as substituents into the molecule of butadiene are far from complete. Both the α- and the β-methylbutadienes are polymerizable to rubbers. Of the dimethylbutadienes, the $\beta\gamma$- and $\alpha\delta$- are polymerizable; the *gem*-dimethyl compound appears, according to observations of Kyriakides and others,[1] to be polymerizable, but according to a statement of Harries[2] only with difficulty. It would appear that methyl substitution in the terminal positions of butadiene has, compared with such substitution in the middle positions, an unfavorable effect on the ease of polymerization. It would appear, further, from the limited data available, that increase in the number of methyl substituents in butadiene diminishes the ease of polymerization, since $\beta\gamma$-dimethylbutadiene polymerizes less easily than isoprene and $\alpha\delta$-dimethylbutadiene less easily than piperylene.[3] The available information regarding the polymerizability of tri- and tetramethylbutadienes is very meagre. The known trimethylbutadienes ($\alpha\alpha\gamma$- and $\alpha\alpha\delta$-) have not been studied from the point of view of polymerization. From its behavior on distillation, Pribytek[4] considered $\alpha\alpha\delta\delta$-tetramethylbutadiene (diisocrotyl) to show an inclination to polymerize, and it has been mentioned in the patent literature as polymerizable.[5] Lebedeff,[6] however, found it to be practically lacking in ability to polymerize when heated at temperatures up to 250°. Another tetramethylbutadiene which has been described, viz., the $\alpha\alpha\gamma\delta$-compound,[7] has not been studied in regard to polymerization.

In the present investigation the hitherto unknown $\alpha\beta\gamma\delta$-tetramethylbutadiene (3:4-dimethylhexadiene-2:4) has been prepared, by the dehydration of the pinacone, 3:4-dimethylhexandiol-3:4, and been found to show little or no tendency to undergo thermopolymerization: when heated under conditions known to produce a greater or smaller amount of a rubber from such dienes as isoprene and $\beta\gamma$-dimethylbutadiene, it suffered no change. Sulfuric acid converted it into a dimer, and air, while bringing about autoöxidation, produced a certain increase in molecular magnitude.

The pinacone, 3:4-dimethylhexandiol-3:4, was prepared from methylethyl ketone by an improved reduction procedure, using amalgamated magnesium, and diluting the ketone with benzene. Conversion of the glycol into a hydrocarbon, C_8H_{14}, was effected by distillation with a drop of dilute sulfuric acid. Now,

[1] Kyriakides, *J. Am. Chem. Soc.*, **36**, 987 (1914); *German Patent* 235,686; Hoffman, *J. Am. Chem. Soc.*, **49**, 530 (1927).

[2] "Untersuchungen über die natürlichen und künstlichen Kautschukarten," 250 (Berlin, **1919**).

[3] Lebedeff, *J. Russ. Phys.-Chem. Soc.*, **45**, 1377 (1913).

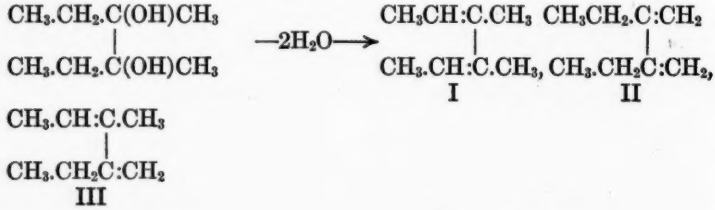
[4] *J. Russ. Phys.-Chem. Soc.*, **20**, 506 (1888); Absts. **1889**, 362.

[5] *German Patent* 235,686.

[6] *Loc. cit.*

[7] Abelmann, *Berichte*, **43**, 1586; Auwers and Eisenlohr, *J. prakt. Chem.*, **84**, 5 (1911).

dehydration of the glycol might conceivably give rise to any or all of the three dienes shown below:



That the product, or at all events the major portion of it, had the structure I was proved by the observation that on oxidation acetic acid free from admixture with propionic acid was obtained. It would thus appear that in the dehydration of the pinacone the ethyl groups take part in preference to the methyl groups. This is in accord with two similar cases on record, viz., (1) the dehydration of dimethyldiethylbutindiol, $CH_3CH_2.CMe(OH).C \vdots C.C(OH)Me.CH_2CH_3$, which gives dimethyloctindiene, $CH_3CH:CMe.C \vdots CCMe:CHCH_3$,[8] and (2) the dehydration of ethylbutinol, $CH_3CH_2.CMe(OH)C \vdots CH$, which gives methylpentinene, $CH_3CH:CMeC \vdots CH$.[9]

An unsuccessful attempt was made to synthesize 3:4-dimethylhexadiene-2:4 by the action of magnesium on 2-bromobutene-2, Me.CH:CMeBr, the chief result of the reaction being a dimolecular product, $C_{16}H_{34}O$.

Experimental

3:4-Dimethylhexandiol-3:4.—The reduction of methylethyl ketone to this glycol was effected by Lawrinowitsch[10] by means of sodium amalgam and by Friedel and Silver,[11] by Herschmann,[12] and by Norris and Greene[13] by means of sodium and moist ether. The yield by the latter agent was, however, only 11 to 14%. Later, aluminum amalgam, magnesium amalgam, aluminum and mercuric chloride, and magnesium and mercuric chloride were described as reducing agents in this connection, without mention being made of the yield.[14] In the present investigation, in order to determine the most advantageous reduction conditions, twenty-one experiments under different conditions were carried out. The chief results were as follows: (1) Metallic sodium and moist ether gave a low yield (9.5%). This is in agreement with previous workers (*vide supra*). (2) Zinc and iron applied to the ketone diluted with benzene gave no yield. (3) Aluminum and magnesium are both capable of giving yields of the order of 40%, but magnesium is the more convenient, as reduction with it requires at most 2–3 hours, whereas with aluminum it requires up to 10 hours at the boiling point of benzene. (4) Previously made amalgams have no advantage over the metal used in conjunction with mercuric chloride. (5) The addition of small amounts of iodine or cuprous chloride[14] does not improve the yield. (6) The amount and character of a diluent influenced the yield as follows: (*a*) By reducing in the presence of excess of ketone after the manner of Richard and Langlais with acetone,[15] the yield was nil. (*b*) Benzene

[8] *German Patent* 241,424.
[9] *German Patent* 290,558.
[10] *Annalen*, **185**, 124.
[11] *Vide* Herschmann, *Loc. cit.*
[12] *Monatsh.*, **14**, 237 (1893).
[13] *Am. Chem. Jour.*, **26**, 293 (1901).
[14] *German Patents* 251,330–1.
[15] *Bull. Soc. Chim.*, **1910**, 455.

is a suitable diluent, but too large a volume affects the yield prejudicially, because the mercuric salt is precipitated unchanged and amalgamation is consequently slower.

The conditions which gave the best yield (41%) of crude oil boiling at 120–135°/55 mm. were as follows: A mixture of 1 equivalent of magnesium clippings or shavings (powder is less satisfactory, as it tends to form a lump), a solution of 0.0747 mol. mercuric chloride in 2.22 mols. methylethyl ketone, and 2.13 mols. benzene was heated on a water-bath under reflux with mechanical agitation until reduction was complete; a further 1.06 mol. benzene being added when the reaction mixture became too stiff to permit of stirring, the magnesium compound was decomposed with ice, and the pinacone salted out with 2 mols. NaOH, dried in benzene solution over NaOH and distilled *in vacuo*. The pinacone was purified by fractionation, the fraction which boiled at 124–7°/55 mm. and which constituted 60% or more of the crude oil being collected. C, 66.2; H, 12.52 (calc.: 65.8, 12.33%). The boiling point at ordinary pressure and n_D^{25} agreed with constants recorded by Norris and Greene.[16]

3:4-Dimethylhexadiene-2:4.—Quantities of 10 to 30 g. of the pinacone were mixed with 1 drop of 20% sulfuric acid, and distilled at a bath temperature of 140–150°. The oil was separated from the water which collected along with it in the receiver; it was dried by leaving it for several days with calcium chloride in a sealed, evacuated ampoule, and was fractionated under reduced pressure. The yield of crude product amounted in one case to 84%. The crude oil gave the following data: C, 86.3; H, 13.17; mol. wt., 108.3 (mean of 6 determinations, 99.8 to 113.6, cryoscopically in benzene) (calcd. for C_8H_{14}: 87.26, 12.73, 110). The pure diene obtained by fractionation under 100 mm. pressure gave the following results: boiling point, 132–4°, 71–3°/100 mm.; n_D^{25}, 1.4630; $d_4^{19.2}$, 0.7832; C, 86.8; H, 12.95; mol. wt. (cryoscopically in benzene), 111.8. When brominated in solution at 0° it took up two atoms of bromine (experimental figure, 2.085). On prolonged standing at 20°, approximately four atoms of bromine went into reaction, but HBr was evolved at the same time. The dibromide was obtained as an oil by evaporating the solvent *in vacuo*. It could not be caused to crystallize. On keeping at 20°, it gradually underwent decomposition, with the formation of colored products.

The molecular refraction of the diene was 38.78. The calculated value using the constants obtained by Conrady[17] is 38.1. The exaltation, 0.68, is of the same order as that found for isoprene, $\beta\gamma$-dimethylbutadiene and other diolefines in which substitution occurs between the conjugated groups, and is less than the values found for such dienes as pentadiene and hexadiene.

Oxidation of a sample of diene boiling at 71–3°/100 mm. was carried out in aqueous suspension by permanganate solution of such a concentration (3%) as to split the compound at the double bonds and completely oxidize the various residues to simple acids. Sufficient permanganate was used to destroy any formic acid which had been produced. When oxidation had come to an end, the solution was filtered; the filtrate was neutralized with nitric acid; excess silver nitrate was added, and the solution was evaporated under reduced pressure to the point of crystallization. Four crops of crystals collected showed the following silver contents: 64.2, 64.3, 64.3, 64.25 (calcd. for CH_3COOAg: 64.7%). Another sample of diene boiling at 72.3°/100 mm. gave on oxidation crops of silver salt containing 64.6, 64.8% Ag.

It is possible that the crude diene contained a proportion of a structural or

[16] *Loc. cit.*

[17] Cf. Auwers and Eisenlohr, *J. prakt. Chem.*, **82**, 65 (1910).

geometrical isomer, as fractions collected a few degrees either side of the boiling point gave similar results to the pure diene on ultimate analysis and for molecular weight, but differed somewhat in refractive index and on oxidation yielded a silver salt containing about 1% less silver than silver acetate.

The diene did not undergo thermopolymerization readily or at all when heated in tubes sealed at about 28 mm., as the following results for three samples show: (*a*) A sample showed after 2 days at 100° a molecular weight of 109.3. (*b*) After 4 days at 100° a sample showed: mol. wt., 109.3; n_D^{25}, 1.4631 (originally 1.4625), d_4^{27}, 0.778263 (originally, 0.778263). (*c*) After 2 days at 100° a sample showed a molecular weight of 111.3, and n_D^{25}, 1.4661 (originally, 1.4660). On allowing a sample of the diene to stand for several months over metallic sodium, the latter was found to dissolve without evolution of hydrogen, and a gelatinous substance was formed, which when treated with alcohol assumed the character of a resin. The diene on washing and drying was found to be unchanged; n_D^{25}, 1.4636 (originally 1.4631).

On dissolving a sample of the diene in concentrated sulfuric acid and then precipitating it with water, it was found to be changed from a thin oil to a viscous liquid, boiling at 170–200°, and n_D^{25} had risen from 1.4650 to 1.4915. This product is probably an impure dimer, C, 85.4; H, 12.69.

When shaken with an aqueous solution of sulfur dioxide, the diene, unlike isoprene and dimethylbutadiene, does not yield a solid, but merely becomes heavier than water, apparently by dissolving sulfur dioxide.

When exposed to the air the diene underwent autoöxidation to a gummiaceous oxidation polymer. A sample allowed to stand for a week or more with limited access of air became transformed into a colorless gum, which, after extraction with methyl alcohol to remove by-products, gave the following results: C, 67.1; H, 10.01%; mol. wt. (cryoscopically in benzene), 640 (calc. for $(C_8H_{14}O_2)_5$:67.65, 9.85, 710). The material, which was soluble in ether, gave a strong peroxide reaction with hot titanic acid, although it gave a negative result with KI.

The diene described above is apparently different from that of the same empirical formula which Herschmann[18] obtained as a by-product on heating 3:4-dimethylhexandiol-3:4 for several hours with 5% sulfuric acid. Herschmann's product boiled at 117–121°, absorbed four atoms of bromine from solution in a freezing mixture, and on autoöxidation gave an oil, $C_8H_{14}O_2$, boiling at 200–230°.

Attempted synthesis of 3:4-dimethylhexadiene-2:4. 2:3-Dibromobutane.—Attempts to brominate *n*-butyl bromide by Reboul's method,[19] *viz.*, exposure to light in the presence of bromine and water, gave negligible yields after several weeks. Linnemann's bromination procedure[20] gave a yield of 15.5% of a dibromo compound, probably 1:3- or 1:2-, boiling at 170–180°. The use of iron wire[21] as a catalyst in conjunction with Reboul's method gave a 32.6% yield of dibromide, boiling at 158–161°, i. e., the 2:3-compound.[22] The dibromide obtained by Reboul without a catalyst boiled at 166°, i. e., it was the 1:2-compound.[23] It is clear that the iron catalyst causes isomerization during bromination.[24] *3-Bromobutane-2.* In preparing this from the dibromide it was found best to use an excess of potassium

[18] *Montash.*, **14**, 233 (1893).

[19] *Bull. soc. chim.*, **7** (3), 124 (1892).

[20] *Annalen*, **161**, 199 (1872).

[21] Cf. Herzfelder, *Berichte*, **36**, 1257 (1893).

[22] Wurtz, *Annalen*, **144**, 234.

[23] Grabowsky and Saytzeff, *Annalen*, **179**, 330.

[24] A recent example of a similar isomerization is the conversion of 1:4 dibromobutane to 1:2:3-tribromobutane with iron and bromine (Braun, *Berichte*, **55**, 3526 (1922); cf. Meyer and Miller, *J. prakt. Chem.*, **46**, 181 (1892).

hydroxide when following the method of Wislicenus,[25] since otherwise some dibromide remained unchanged, owing to the formation of some butine as a by-product. Two hundred sixty-three grams dibromide, 82 g. KOH, and 400 cc. methyl alcohol gave 124.7 g. (75.8%) of the high-boiling modification of the bromobutene, b. p. 89–93°; Br, 57.3%; mol. wt., 133.7 (calc. for C_4H_7Br: 59.3, 135).

The bromobutene was now treated in dry ether with magnesium in the presence of iodine as a catalyst. It was found to dissolve only one-half atom of magnesium. On decomposing with ice and dilute acetic acid and distilling the ethereal solution, there was obtained no trace of the desired diene, but, besides unchanged bromobutene, an oil with an irritating, onion-like odor, b. p. about 160°, n_D^{25} 1.4735, C, 80.2, H, 13.82%, mol. wt. (benzene), 208.2 (calc. for $C_{16}H_{34}O$: 79.3, 14.05%, 242).

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[25] *Annalen*, **253**, 231 (1889).

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Some Features of Sulfur in Rubber Manufacture

Douglas F. Twiss

Sulfur as a Powder

By a striking coincidence the element sulfur appears to have been associated with rubber as a *dusting* powder, for the removal of tackiness, for a considerable time before its unique vulcanizing power was discovered. The actual incorporation of sulfur into rubber by Goodyear in 1839 is consequently the less surprising, although his discovery and its rediscovery by Hancock lose on that account no whit in importance.

With all compounding ingredients for rubber, fineness of division is an important and desirable characteristic, and it is often assumed that the desirable degree of fineness is limited only by the cost of production. Sulfur, however, is exceptional in that for ordinary use with rubber the *optimum limit of fineness* of division can easily be exceeded. Very finely divided sulfur—probably on account of the known depressing influence of fineness of division of a substance on its melting point—often tends to cake undesirably during the mixing operation, and so may actually lead to an impaired dispersion relative to that obtainable with less finely powdered material.

In spite of this limit to useful expenditure on further disintegration of sulfur for ordinary "dry mixing" with rubber, it must be admitted that such finely dispersed forms as *milk of sulfur* or *precipitated sulfur*, and various *colloidal sulfurs* are applicable with especial advantage in many of the newer "latex processes." Small particle size here is favorable to the production of more stable suspensions or to the avoidance of settling. For the production of vulcanized latex, indeed, finely divided sulfur is particularly desirable; not only is the suspension of the particles here of importance, but also a fairly uniform distribution or partition among the rubber globules. Otherwise the vulcanized state may be attained by relatively few of the globules.

Flowers of sulfur (i. e., genuine sublimed flowers) is a natural mixture of the crystalline *soluble* variety of sulfur with up to 30 per cent, or even more, of the amorphous variety *insoluble* in carbon disulfide. When freshly prepared it has a relatively fine state of division and the microscope reveals curious chains of linked spheroidal particles; on prolonged storage, however, these gradually disappear with development of a completely crystalline appearance, the crystalline particles having grown at the expense of the amorphous ones. Probably on account of the presence of the less stable variety, flowers of sulfur also shows a greater tendency to become acidic by oxidation in storage than the pulverized crystalline sulfur. Flowers of sulfur during dry mixing with rubber is particularly liable to lead to caking doubtless, in part, on account of the presence and amorphous character of the minor component and the consequent depressing effect on the melting point of the other.

For ordinary purposes in rubber manufacture powdered crystalline sulfur is generally satisfactory. For satisfactory dry mixing an average particle size of 0.02 mm. (e. g., 0.004–0.030) is sufficient in normal circumstances. If required for

latex purposes it can be reduced to the condition of colloidal dispersion in water by means of an effective colloid mill and a suitable protective colloid.

Sulfur as a Solute

A fact of the greatest importance in rubber manufacture is that sulfur dissolves readily in warm rubber. But for this property the production of uniformly vulcanized rubber would be a matter of very great difficulty. Whereas, however, the customary dry mixing operation may yield a visibly coarse dispersion of sulfur, the first important effect of the heat applied for vulcanization purposes is the formation of a uniform solution of sulfur in rubber; as far as concerns these components vulcanization of soft rubber consequently ensues in a single phase system.

Solubility of Sulfur.—Although today the evidence appears to be fairly plain, the question whether free sulfur in rubber is in a state of mere solution or is more or less adsorbed was earlier a contentious one (see, e. g., Loewen, *Z. angew. Chem.*, **25,** 1610 (1912)). It is remarkable, however, that the simultaneous presence of carbon black in unvulcanized rubber seriously interferes with the removability of free sulfur; in this case, however, adsorption by the carbon black may be a complicating factor.

Although the *solvent power of rubber* for sulfur was realized earlier by C. O. Weber and others, some of the first work from a quantitative aspect was by H. Skellon (*India Rubber J.*, **46,** 251 (1913)), who adduced evidence that in the heat-vulcanization process the first stages are (*a*) successive dissolution of the sulfur and uniform dispersion of the solute (preceded commonly by melting) in the rubber, and (*b*) slow chemical combination of the two materials. He also showed (*ibid.*, p. 723) that the solvent power of vulcanized rubber for sulfur is greater than that of raw rubber.

The observed fact that the rate of combination of rubber and sulfur follows a straight line course (instead of the usual curvilinear one for such binary chemical reactions) for original mixtures containing up to about 10 per cent of sulfur and not above (*Rubber Industry*, **4,** 172 (1914)) Skellon attributed to the fact that this limit represents the approximate maximum solubility of sulfur in rubber under the conditions.

Further determinations of the *solubility of sulfur* in rubber have been made by C. S. Venable and C. D. Green (*J. Ind. Eng. Chem.*, **14,** 319 (1922)) and, more exactly, by W. J. Kelly and K. B. Ayers (*Ind. Eng. Chem.*, **16,** 148 (1924)). Even the results of the latter investigators, however, cannot claim a high degree of accuracy for the degree of solubility of sulfur in rubber; for on account of the experimental conditions their figures at higher temperatures are probably too small. The former worked by the analysis of the solution obtained on keeping rubber (already mixed with sulfur if desired) in contact with powdered sulfur at various temperatures until the attainment of equilibrium. They made the important comment that, contrary to other views expressed earlier by Skellon, C. O. Weber ("Chemistry of India Rubber," p. 112) and others, the non-blooming of ebonite goods is to be explained by the greater resistance of such material to migration of the free sulfur rather than by its greater solvent power for sulfur or by its abnormal colloidal structure.

Kelly and Ayers tackled the problem in two distinct ways, viz., by finding the concentration conditions of the final equilibrium state when (1) a mixture of rubber and sulfur is kept in a sulfur-solvent such as amyl alcohol, and (2) rubber is kept in a saturated solution of sulfur in butyl alcohol.

The analytical results revealed the validity of the simple partition law, viz., that at equilibrium for any temperature

$$\frac{\text{Concentration in rubber}}{\text{Concentration in other solvent}} = \text{constant},$$

thereby proving that (*a*) the sulfur in the rubber is merely in a state of solution and not of adsorption, and (*b*) the sulfur has the same molecular weight in the two media, viz., rubber and the alcohol. The solubility observed ranged from approximately 1 per cent in raw rubber at 30° up to approximately 6 per cent (to 100 of rubber) at 75° in rubber with a coefficient of vulcanization near 17. Solubility increases with temperature and also with degree of vulcanization.

Effect of Solubility of Sulfur in Rubber.—The preceding considerations show that the relation of rubber to its free sulfur are the ordinary ones of solvent to solute, and that *blooming*, as has long been recognized, is the surface crystallization of a supersaturated solution. The following details can be deduced and are in accord with experience.

A. Since the solubility of sulfur at the ordinary temperature is about 1 per cent, mixtures or vulcanizates containing less than 1 per cent of free sulfur (to 100 of rubber) should not bloom markedly in normal circumstances.

B. Factors leading to the development of surface crystals or causing contamination of the surface with sulfur dust will favor marked surface crystallization or blooming, e. g., (1) rapid surface cooling; (2) contact of the warm rubber with dust containing sulfur, e. g., on tables, liners, or human fingers; (3) high temperature of batch during mixing which causes complete dissolution of sulfur and leaves no nuclei to start internal crystallization.

A calender worker with moist hands is particularly likely to get sulfur dust on his fingers and so to cause fingerprints to bloom on rubbered sheet. Sulfur dust is to be found everywhere in a rubber factory.

C. Factors favorable to *internal* crystallization will militate against surface blooming, e. g., (1) cool conditions of mixing so as to prevent complete dissolution of the sulfur, the undissolved particles serving as nuclei for internal crystallization; (2) not too fine sulfur; (3) a high proportion of sulfur (which at first sight seems paradoxical) so as to ensure a residue of undissolved sulfur; (4) the intentional introduction of relatively insoluble crystalline particles isomorphous with rhombic sulfur, e. g., selenium, which will constitute relatively permanent nuclei for the subsequent internal crystallization of the sulfur on cooling; (5) use of flowers of sulfur containing a proportion of insoluble sulfur, which will give uncured stock with less tendency to bloom than similar stock with soluble sulfur; after vulcanization, however, the difference disappears, because insoluble sulfur as such does not survive vulcanization. (See p. 350.)

D. Blooming will be less marked in stocks kept at a uniform temperature.

The solubility of sulfur in rubber has many *advantageous consequences* for the rubber manufacturer. Desulfurizing, except for the thinnest of sheets or the smallest of fragments, would be impossible except for the fact that the dissolved sulfur migrates to the surface and so assists in its own removal; the higher the temperature the greater the solubility (especially if the melting point of sulfur is exceeded) and also the greater the migration velocity. This solvent power of rubber for sulfur, indeed, has been the subject matter of a patent for the removal of sulfur from rubber solutions employing a sheet of vulcanized rubber as a semipermeable membrane (Debauge, *German Patent* 244,712).

The migration of dissolved sulfur plays an important part in enabling strong attachment in "built up" goods in which different mixings are superposed in layers. In these, during vulcanization, sulfur migrates from a sulfur-rich layer into the

contiguous surface of a sulfur-poor layer, the result being a graded joint with increased mechanical strength against separation.

The greater solubility of sulfur in vulcanized rubber than in unvulcanized has two consequences of practical interest: firstly, the presence of reclaimed rubber reduces any tendency to blooming, and, secondly, the free sulfur in a vulcanized mixing containing carbon black is much more easily removed (e. g., by acetone) than the free sulfur in the same mixing before vulcanization.

In closing this section two *disadvantages* arising from the solvent power of rubber for sulfur may be mentioned. If a film of rubber solution containing sulfur is applied to a rubber surface, e. g., the end of an unjoined vulcanized motor tube, care should be taken not to delay the subsequent vulcanization operation too long. Much of the sulfur applied in the solution may otherwise be lost by migration into the supporting surface with consequent impairment of the character of the final vulcanized film. A similar loss may occur with an organic accelerator, and the position is doubly serious. In an actual case of a solution of a mixing containing 3.3 per cent of sulfur, a film applied to a layer of vulcanized rubber showed after 24 hours only 0.9 per cent of sulfur, although a film on glass gave the full sulfur content. In another case a pad of rubber mixing about 0.5 mm. in thickness adjacent to the tread of a motor cover contained originally $7^1/_4$ per cent of sulfur, but on subsequent removal from the cover after vulcanization contained only a total of $5^1/_2$ per cent.

The inverse of this migration loss of sulfur has been described by Pestalozza and others (*India Rubber Journal*, **65**, 238 (1923)) for the introduction of sulfur into mixings containing ultra-accelerators, thereby deferring contact of accelerator and sulfur until the last moment, and so preventing prevulcanization.

Finally, but for its tendency to bloom, sulfur might have been an ideal cheap filler for rubber. It has a low specific gravity, it has no softening effect on the rubber, it is cheap, and it is already an essential ingredient.

Sulfur and Its Modifications

Of all the substances used in rubber manufacture, sulfur is doubtless the one which occurs in the greatest number of different forms. As already mentioned incidentally, the temperature conditions obtaining in some operations are above the melting point of sulfur. In any mixing indeed under ordinary vulcanizing conditions undissolved free sulfur must be reduced to the fluid state. Hancock's method of vulcanization by immersion in a *molten* sulfur bath is still also in practice.

Sulfur occurs also in the *vapor* state in much greater quantities than might be expected. Incrustations of sulfur, arising from the condensation of vaporized sulfur, are commonly observable in dry heat vulcanizing chambers, and in enclosed driers for spread or soaked fabrics; they occur sometimes even inside extruding machines, where their presence may not be suspected until evidence is forthcoming of an undesirable character.

The vapor pressure of sulfur at "rubber temperatures" has been measured experimentally by various investigators with results not always in very close accordance. The vapor pressure curve given in Figure 1 has been derived from that of mercury by making use of Ramsay and Young's law, which states that, at corresponding temperatures, the respective vapor pressures of mercury and sulfur will be the same.

$$\frac{\text{Temperature (abs.) of vap. press. P for sulfur}}{\text{Temperature (abs.) of vap. press. P for mercury}} = \frac{\text{B. pt. (abs.) of sulfur}}{\text{B. pt. (abs.) of mercury}} = \frac{273 + 444.5}{273 + 357.25}$$

The results indicated by the curve are in satisfactory agreement with the best of the available experimental data and are more continuous over any desired range. With the aid of such a vapor-pressure curve and the knowledge that sulfur vapor below 300° C. is mainly octatomic, it is possible easily to calculate the maximum weights of sulfur which can vaporize into a definite volume of air or other gas at different temperatures.

TABLE I

Temperature	Wt. of sulfur vapor in 1000 cu. ft. of saturated space
120° C.	0.5 oz.
150° C.	4 oz.
180° C.	1 lb.

In addition to the above three states, sulfur also gives alternative forms both in the liquid and solid conditions. The liquid allotropic forms as distinct from the

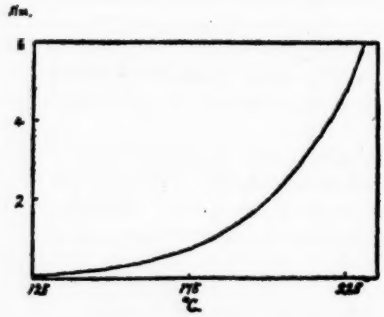

Figure 1

corresponding solid forms do not affect the rubber industry seriously, but the solid *allotropic modifications* have been to the rubber chemist and technologist a subject of much interest, speculation, and even contention for many years.

Rhombic and prismatic sulfur are merely interconvertible different crystalline forms the transition temperature of which, under ordinary conditions, is about 95.5° C. Below this temperature the rhombic form is more stable and less soluble. Vulcanized rubber containing residual free sulfur in the well-known feathery aggregates of prismatic sulfur (or in the form of "super-cooled" molten sulfur, can, therefore, show "blooming" by gradual migration of this more soluble sulfur to the surface, where it crystallizes as the less soluble rhombic sulfur. Internal nuclei for the prevention of blooming should, therefore, be isomorphous with rhombic sulfur as, indeed, selenium is.

There are, however, several distinct varieties of solid sulfur of different intramolecular structure; only some of these need to be considered particularly in the present connection. The most important are (*a*) S_λ represented by ordinary crystalline sulfur whether rhombic or prismatic, (*b*) S_μ represented by the insoluble constituent of flowers of sulfur, (*c*) S_π present to some extent as a minor constituent in ordinary sulfur (e. g., approximately 3 per cent at the melting point), the proportion varying with the conditions, rise in temperature, for example, being favorable to its further formation.

The remarkable elasticity of *plastic sulfur* (of which the most important constituent is S_μ), obtained by heating sulfur to 180° or higher and cooling quickly, has naturally prompted tentative association of this form of sulfur with rubber.

It has been suggested that the effect of vulcanization may be caused by the congruence of the elastic properties of rubber and of plastic sulfur in the same material (M. Kröger, *Kolloid-Z.*, **33,** 267 (1923)). The similarity, although striking, is probably nothing more than a coincidence.

Much also has been made of the fact that alkaline substances such as accelerated vulcanization also act as catalysts towards the changes represented by the equations:

$$S_\lambda \rightleftharpoons S_\pi \ (\longrightarrow S_\mu)$$
$$S_\lambda \rightleftharpoons S_\mu$$

This parallelism has led repeatedly to the suggestion that such equilibria play a fundamental part in the vulcanization process. G. van Iterson (*Comm. Netherland Govt. Inst. Rubber Ind.*, **7,** 257 (1916)), L. Stoll (*Rubber Age*, (N. Y.), **17,** 418 (1925)), and quite recently again H. Dannenberg (*Kautschuk*, **1927,** 104 and 128) and P. Scholz (*ibid.*, **1927,** 101 and 127) have propounded a view that S_π or S_μ is the form of sulfur active in vulcanization, and that organic accelerators are effective by expediting its formation from S_λ. Apart from the fact that other theories are available for the mode of action of organic accelerators (e. g., W. Scott and C. W. Bedford, *J. Ind. Eng. Chem.*, **13,** 125 (1921), C. W. Bedford and L. B. Sebrell, *ibid.*, **13,** 1034 (1921); **14,** 25 (1922)), definite evidence against the above view has been brought forward by the writer (*J. Soc. Chem. Ind.*, **1917,** 787; *Annual Repts. Soc. Chem. Ind.*, **1919,** 327; Twiss and Thomas, *J. Soc. Chem. Ind.*, **1921,** 48T). The following includes additional evidence.

The progress of acetone-extraction of sulfur from the following mixtures has been determined: (*A*) 100-rubber, 10-S_λ; (*B*) 100-rubber, 10-S_μ (S_μ extracted from flowers of sulfur); (*C*) *A* after vulcanization for 120 min. at 40 lbs.; (*D*) *B* after vulcanization for 120 min. at 40 lbs.

The remarkable difference in the behavior of the unvulcanized mixings was repeatedly confirmed, but only a typical experiment is quoted in Table II. The type of continuous extraction apparatus used was such that the sample (6 g.) was throughout kept at the boiling temperature of the pure solvent.

TABLE II

Period of extraction, hours	Total weight of sulfur extracted (from 6 g.) A	B	C	D
1	0.101	0.017	0.232	0.198
2½	.254	.034	.388	.358
5	.424	.071	.444	.410
10	.529	.150	.449	.474
20	.540	.315	.450	.477
30	..	.372	..	.478
40	..	.407	..	..
50	..	.419	..	..
60	..	.433	..	..

For more convenient scrutiny the above figures are plotted in Figure 2.

The results of the above and earlier experiments may be summarized thus: (i) S_μ is not appreciably more effective than S_λ as a vulcanizing agent; in the above experiments the degree of vulcanization is substantially the same. (ii) S_μ at ordinary vulcanization temperatures changes very rapidly into S_λ.* The free sulfur in Sample D is removed at about the same rate as for C, and more rapidly than that from A, showing that it migrates to the surface by its solubility.

* So easily does S_μ change into S_λ that a mixture S_μ, rubber, an ultra-accelerator and zinc oxide in a solvent gels almost as soon as one containing S_λ instead of S_μ.

The curves C and D relative to A incidentally reveal the greater solvent power of rubber after vulcanization. (iii) As shown earlier (Twiss and Thomas, *loc. cit.*) the regularity of increase in the rate of vulcanization with rise of temperature indicates that between 60° and 188° C. the increasing proportion of S_μ and S_π relative to S_λ has no marked exalting effect on the rate of vulcanization.

Evidence (iii) also controverts a theory elaborated by L. E. Weber ("Chemistry of Rubber Manufacture," pp. 88–92), in which the assumption is made that only S_2 molecules can effect vulcanization, and the increase in rate of vulcanization with rise of temperature is attributed solely to the increasing proportion of S_2 in the equilibrium $S_8 \rightleftharpoons 4S_2$. The theory possesses, however, so many other points of weakness, that it need not be considered further here. The evidence, indeed, indicates that whatever allotropic forms may be present in equilibrium in sulfur under normal conditions, they are *remarkably little divergent in activity towards rubber.*

In reviving what may be termed the S_μ theory of acceleration, however, Dannenberg (*loc. cit.*) has gone further and propounded a theory that not only is S_μ exceptionally active in vulcanization, but that the vulcanized

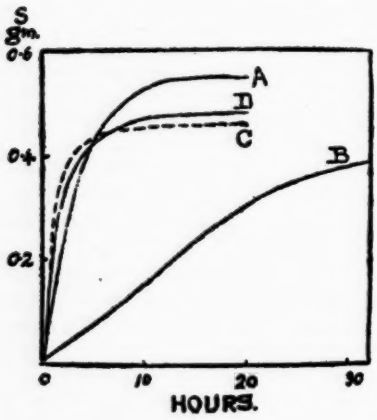

Figure 2

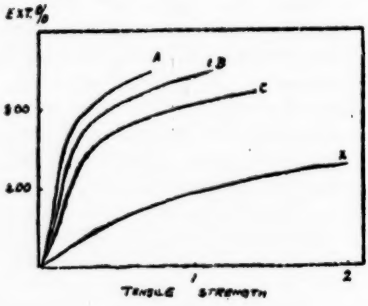

Figure 3

product is merely a colloidal dispersion of S_μ in raw rubber.

The evidence against such a view at present is overwhelming. (1) The mixing of 10 per cent of finely divided S_μ into rubber does not cause the slightest sign of vulcanization. (See above.) (2) Vulcanization proceeds at substantially the same rate in S_λ and S_μ mixings of otherwise comparable composition. (3) S_μ is incapable of withstanding vulcanizing conditions. This result, indeed, is in accord with the well-known tendency of S_μ to undergo very rapid conversion into S_λ even at 120° C. (E. Beckmann and others, *Z. anorg. Chem.*, **102,** 201 (1918); **103,** 189). (4) As shown by A. M. Kellas (*Trans. Chem. Soc.*, **113,** 903 (1918)), S_μ is not formed to any appreciable extent in S_λ below 170° C. (5) Devulcanization in the sense of the removal of "combined sulfur" is not yet possible. If the "combined sulfur" merely consisted of S_μ, treatment with hot alkali solution would readily effect complete devulcanization.

Indeed, the position may be summarized by saying that although S_λ has been stated to be a little more active than S_π towards silver, at the present time there is no evidence to associate any one of the above-mentioned allotropic forms of sulfur more than another with the mechanism of vulcanization.

A further modification of sulfur is the very active and unstable form which is the

agent in the Peachey process. This can best be described by the non-committal term, *nascent sulfur*. Nascent sulfur is also the active substance in the use of ammonium polysulfide as a vulcanization agent for latex. The effect of organic accelerators also can be explained by their ability to convert sulfur into the nascent active condition. It is also well known that vulcanization of a mixture of rubber and sulfur can be induced by exposure to sunlight or ultra-violet radiation, the process sometimes being described as "solarization." The effect has wrongly been attributed to S_μ, which is formed when S_λ is exposed in solution to ultra-violet radiation. It is probable that nascent sulfur occurs at an intermediate stage in this conversion of S_λ (probably S_8 molecules) into S_μ (probably S_6 molecules), and that this nascent sulfur is the cause of the vulcanization.

Is Vulcanization a Reinforcement? Some years ago, however, the writer (*J. Soc. Chem. Ind.*, **1925,** 106T; *India Rubber J.*, **65,** 607 (1923)) and others directed attention to the possibility of explaining many of the effects of vulcanization by the formation of a fine *colloidal dispersion* of a proportion of a *rubber-sulfide* compound or compounds in a matrix of unvulcanized rubber. The supporting evidence is very considerable. This effect is probably accompanied by a chemical alteration or polymerization of part of the rubber hydrocarbon itself induced (as such changes can be) by the concurrent reaction of a small part of the rubber with sulfur.

Briefly, the supporting evidence may be summarized thus: (1) There is no strict proportionality between the coefficient of vulcanization and the physical result (cf. Shepard and Krall, *J. Ind. Eng. Chem.*, **14,** 951 (1922)). (2) The proportion of sulfur (e. g., 1–5 per cent) necessary for vulcanization to soft rubber is quite insufficient for the complete conversion of rubber into any simple rubber-sulfur compound. (3) Raw rubber heavily compounded with carbon black (e. g., rubber 100, black 40) is insoluble in ordinary rubber solvents, and, as recently shown by P. Stamberger (*Gummi-Zeitung*, **41,** 214 (1927)), the swollen product possesses other characteristics of a swollen gel of lightly vulcanized rubber. If the carbon could be *produced* inside the rubber, the effect would be still more marked. The "rubber-sulfide" dispersion in rubber must be even finer and have a still more intense effect. (4) Factors favoring a finer dispersion of the "rubber-sulfide" compound, such as more rapid formation, e. g., by use of an accelerator, tend to the production of stronger or more effectively reinforced products. (5) Factors favoring growth of such dispersed particles, e. g., prolonged heating, lead to gradual softening of the rubber, that is, to decreased reinforcement, e. g., in ordinary "reclaiming," where the chemical degree of vulcanization is not substantially reduced. (6) By extraction it is possible from vulcanized rubber to separate fractions containing less combined sulfur than the residue.

In Figure 3 is given a set of physical stress-strain curves.

X is for rubber vulcanized to a coefficient of about 3, but containing also (as the only other ingredient) 40 per cent of carbon black (to 100 of rubber). A, B, C are curves for a plain rubber sulfur mixing of different degrees of vulcanization. It will be seen that the introduction of the carbon black has effected a change in the course of the stress-strain curve of the same type, and in the same direction, as that produced by an increase in the degree of vulcanization. Curve X, however, could not be attained by direct vulcanization of a rubber-sulfur mixing, because long before the position of Curve X was attained the product would be hopelessly overcured.

Comparison of the position of the curves, indeed, leads by a rough calculation to the result that if progressive vulcanization were possible to the position of Curve X the required coefficient of vulcanization would be roughly 10. In other words,

the effect of such an ingredient as carbon black enables the alteration of the physical condition of the rubber (as revealed by the stress-strain curve) in the same direction as would be produced by further vulcanization, but to a much greater extent than is possible by ordinary vulcanization without simultaneous undesirable effects.

The view that some chemical combination of rubber and sulfur occurs in vulcanization is today generally accepted. As to the molecular composition of the products, except $C_{10}H_{16}S_2$, the essential constituent of hard rubber or ebonite, little is known. It is of interest that recent investigation of the changes in various physical characteristics, e. g., in the density and electrical properties, with progressive vulcanization, suggests the probable existence of $(C_5H_8)_2S$ and gives possible indications of others (McPherson and others, *U. S. Bureau Standards, Sci. Paper* **560,** 383 (1927)). In the light of the foregoing discussion it is the reinforcing effect of such compounds, in a state of colloidal dispersion, which causes the improvement of the tensile properties in vulcanized rubber.

Is Sulfur Indispensable?

At the present time no agent is superior to sulfur or even a satisfactory substitute for sulfur in vulcanization. If, however, it be assumed that the reinforcing effect of carbon black is of the same character as vulcanization, this statement must be qualified by the addition of the words "for certain ranges of vulcanization."

From the natural grouping of the chemical elements into series of similar chemical properties, it might be expected that the adjacent elements in the sulfur group, viz., selenium and oxygen, would be capable of affecting rubber in a similar manner to sulfur. *Selenium* (I. Williams, *Ind. Eng. Chem.*, **15,** 1019 (1923), and C. R. Boggs and E. M. Follansbee, *Trans. Inst. Rubber Industry*, **2,** 272 (1926)) is, indeed, capable of vulcanizing rubber, although, as might be expected from its higher atomic weight, its action is more sluggish than that of sulfur. It can be assisted by organic accelerators, however. As an alternative it has been suggested that selenium should be used in conjunction with sulfur, thereby not only insuring the additive effect of the sulfur and the selenium, but also taking advantage of an accelerative influence exerted by the selenium on the action of the sulfur. Selenium can also reduce the tendency to blooming of sulfur in the vulcanized product. A further claim has been made, however, that the incorporation of selenium (e. g., $^1/_2$–$1^1/_2$ per cent) causes a marked increase in the abrasion-resistance of carbon black mixings (Bierer and Davis, *India Rubber J.*, **71,** 570 (1926)). This would be a most important matter for the manufacture of goods which have to withstand mechanical wear. Unfortunately experiments put in hand by the writer, even reproducing the described tests as closely as possible, have failed to reveal any justification for the claim as to wonderful improvement in the resistance to abrasion, only small irregular differences being observed such as would be within the range of unavoidable error of experiment. This disappointing result appears not to be an isolated one, but to have been the experience of others who likewise have endeavored to reproduce the startling advantages stated in the original claims.

Oxygen, as an adjacent element to sulfur in the periodic table, would be expected in like manner to be chemically active towards rubber. Unfortunately its action generally does not lead to desirable results. Although the use of benzoyl peroxide as a vulcanizing agent is doubtless associated with the activity of the oxygen atoms of this substance, the results, although modified by the benzoyl radical, are relatively unattractive. With this possible exception, indeed, it may be said that in the manufacture of soft rubber goods the action of oxygen on rubber is undesirable, and merely a stage towards final destruction. There is, however, a notable degree of parallelism between the action of sulfur and of oxygen. Thus (*a*) both are

irreversible and the rubber cannot be recovered unchanged from the product; (*b*) both actions are autocatalytic (Skellon, *loc. cit.;* Ostwald, *J. Soc. Chem. Ind.*, **1913,** 179); (*c*) the action of both becomes particularly rapid when the rubber hydrocarbon has already undergone combination with about 5 per cent sulfur; rubber in this condition oxidizes with exceptional ease, and also undergoes further vulcanization so rapidly as to be capable of leading to serious internal development of heat (A. A. Perks, *J. Soc. Chem. Ind.*, **45,** 142T (1926)).

As was formerly clearly demonstrated by Loewen (*Z. angew. Chem.*, **25,** 1553 (1912)), the production of soft rubber by vulcanization involves combination of only part of the rubber hydrocarbon with the sulfur, the remainder of the hydrocarbon undergoing modification (in some way at present uncertain) induced by this chemical reaction. From this point of view it is probable that the action of *sulfur chloride* as a vulcanizing agent is not dependent on its character as a derivative of sulfur, but merely on some especial feature of the chemical activity of the sulfur chloride molecule. Although hitherto no chemical agent has been found, the action of which on part of the rubber can induce so marked and beneficial a change in the remainder of the rubber, there is no reason why a substance or substances should not yet be discovered capable of yielding equal or even superior results. Unfortunately, present knowledge provides no definite principle to guide the investigator in this direction, and advance must, for the present, be by merely empirical methods.

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Recent Scientific Advances in Connection with Guayule

David Spence[1]

VICE-PRESIDENT, CONTINENTAL RUBBER COMPANY

RECENT scientific advances in connection with guayule have been made along botanical and biological as well as chemical lines. The work of Dr. W. B. McCallum[2] in definitely identifying many different varieties of guayule and subsequently propagating in California a few selected strains that best respond to intensive cultivation marks a distinct advance in the scientific development of this subject, and his successful efforts in seed selection and propagation will always stand as a monument to his skill and perseverance in this connection. His work is not only of fundamental importance in any study of the effect of environment on natural growth, but also has clearly shown that the available rubber or yield of rubber from the shrub is determined to a large extent by the variety of shrub which is cultivated. The bridge between mariola, with its three per cent of available rubber, and the best varieties of guayule as now growing in California, is apparently spanned by an almost infinite number of varieties of guayule differing in form, size, color, rate of growth, etc., as well as in their hydrocarbon content.

On the biological side, Dr. McCallum's development of young guayule plants from seed was not accomplished as a practical matter until he had discovered and applied chemical and other means of treating the seed to stimulate and

[1]This article comprises the greater part of a paper read before a meeting of the New York Group, Rubber Division, A. C. S., April 25, 1928.

[2]McCallum is botanist of the Continental Rubber Company, of N. Y. An extensive paper by him on the subject of "Botany and Cultural Problems of Guayule," was published in the November 10, 1926, issue of *The Rubber Age* Vol. 20, pp. 129-132).

control its germinating powers. At the present time, it is possible to effect practically a 100 per cent germination of guayule seed, whereas early experiments in this regard had been most discouraging.

In the biochemical and chemical fields, studies have been made on the composition of the shrub, all with the object of intelligently improving the process of extraction and the quality of the resulting rubber. Perhaps the most important scientific as well as practical accomplishment in this connection is the discovery of the fact that the rubber in guayule shrub does not exist in the cells of the rubber plant in the form in which it is recovered, as has been generally believed, but on the contrary is present there largely in the form of a colloidal suspension in the plant juices. Within the individual cells this fine suspension of microscopic globules in a state of rapid Brownian movement can be readily seen with the higher powers of magnification, and the agglomeration and final coagulation of these globules into microscopic particles of rubber by coagulating agencies, such as alcohol, can be followed.

In my paper read before the American Chemical Society in September, 1926,[3] I pointed out the practical significance of these observations. But for the fact that the rubber in the guayule shrub does exist in this dispersed form, the hope of effecting any large improvement in physical or chemical quality would be much less encouraging. However, existing as it does in a more or less disperse condition, even in shrub which has been partially dried, it will be very apparent to every student of colloid chemistry that there is opened up a wide field for profitable investigation. Much has already been accomplished in this connection, but I believe that we are still only on the threshold of important improvements as a result of this observation.

Composition of the Shrub

Turning now to the composition of guayule shrub as we find it both in Mexico and California, obviously there will be a difference in elemental composition, according to the location and variety of shrub investigated, and also according to the climatic conditions at the time the shrub is pulled for investigation. It is impossible, therefore, to speak of the composition of the shrub except in very general terms.

From a practical standpoint, however, the elements of the shrub can be roughly divided into those which are soluble in water (the tannins, water soluble carbohydrates, nitrogen-containing substances and such like), and those which are soluble only after hydrolysis, which include the pectin-

[3]Published in *The Rubber Age*, Nov. 10, 1926 (Vol. 20, pp. 133-135).

like substances constituting the middle lamella of the cell wall and protein or gluco-protein-like substances which are not readily dissolved out by water, and apparently constitute a large part of the plant. There is also the cellulose or fibrous structure of the plant and the bark, both insoluble in water, and not readily hydrolysed, the true resins and resin acids of the plant, insoluble in water, but soluble in acetone, and the rubber itself, which can be extracted more or less quantitatively by means of carbon tetrachloride.

Investigations have shown that the guayule shrub contains on the average about 10 per cent of material readily soluble in water. There is an additional 10 to 15 per cent of materials which become soluble in water only after hydrolysis. They can be decomposed by fermentation into water soluble decomposition products, and consist essentially of carbohydrates on the one hand and vegetable protein on the other. In the milling of the shrub these water insoluble plant products become bound up in the rubber to a greater or less extent, and are responsible, as we have discovered, for the high acetone extract of guayule rubber and for several of its more obvious deficiencies. By decomposition of these carbohydrates, by fermentation into water soluble derivatives, such as sugars, organic acids, carbon dioxide and the like, and by putrefactive decomposition of the vegetable protein prior to milling of the shrub, it is entirely possible to reduce the acetone extract of guayule rubber 60 to 70 per cent, and to improve the vulcanizing properties of the rubber 30 to 40 per cent.

By a process of retting of guayule shrub under suitable conditions and prior to milling, somewhat analogous to the retting of flax, it is possible to reduce the acetone extract of the resulting rubber from 25 to 30 per cent to 9 to 10 per cent. The physical properties on vulcanization of the resulting rubber, on the other hand, if the retting operation is properly carried out, can be so modified that the tensile properties of the rubber may be almost doubled. These are rather astounding results, and it would take me too far afield to go into the researches which have led up to these remarkable discoveries.

That the acetone extract of guayule rubber is only in small part of truly resin character, and is not a definite and unalterable component of guayule rubber, but rather an accidental associate of the same which can be removed to a large extent without resort to the expensive and troublesome operation of extracting the rubber by acetone, by the simple and inexpensive expedient of submitting the shrub to a thorough fermentation before milling the same, has been demonstrated beyond any possible shadow of doubt. In addition, by suitable decomposition by putrefaction of the protein in the shrub, it has been found possible to improve

tremendously the quality of the resulting rubber from the standpoint of its stability and tensile after vulcanization.

These discoveries, which have all been made within the past two years, are now finding definite expression in the production of Ampar[4] rubber. A way has been opened up and means found of completely changing the composition and vulcanizing quality of guayule rubber. That the final word has been said in this direction, I would be the last to predict. I am more inclined to believe that we are only beginning on our development of this product, and that in due course results of still greater importance will be obtained.

It is interesting to note in passing that the treatment to which we now subject the shrub prior to milling is one which, from the early days of the guayule industry, has been regarded as suicidal to quality of rubber. This retting of the shrub causes a more or less complete disintegration of the cell structure of the plant, and results in a product going to the mill very much changed, structurally as well as chemically.

It would take me too far afield to go into the fascinating studies—chemical, bio-chemical and microscopical—which have led up to and followed from this retting of guayule shrub. From the retting liquor, it is hoped in due course to develop products of commercial value, and similarly the other by-products of the plant, the fibre in particular, should find in time some better industrial application than that of a fuel to be burned under boilers.

In regard to the rubber itself, some very interesting studies have been made and are still under way in California to determine the conditions under which the maximum yield and quality are obtained. That there is a seasonal variation in the percentage of extractable rubber from the plant is clearly indicated, but the conditions under which a maximum rubber content is obtained are still a matter of further investigation.

Similarly the quality of the hydrocarbon itself cannot be said to be finally settled until the problems of coagulation and preparation of the rubber from the shrub have been exhaustively investigated and once and for all disposed of. At the present time, the rubber hydrocarbon from guayule, as we have prepared it, appears to more nearly resemble the hydrocarbon from Caucho ball in its physical properties. Whether this is an inherent characteristic of the rubber from guayule, or merely the result of the treatment to which the green shrub is now subjected after it is uprooted and before milling, time and experimentation alone will tell.

[4]Trade name adopted by the Intercontinental Rubber Company.

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Color Reactions of Rubber

H. Pauly *

WHILE the organic chemist, working with comparatively small molecules, can proceed directly by exact methods to an explanation of the structure of compounds, and therefore considers color reactions of minor importance, these reactions often afford a convenient tool for the chemist who is investigating substances of very high molecular weight, which occur for the most part in nature. They offer a quick means of obtaining a preliminary idea of the presence of certain chemical groups, or of distinguishing between substances which can be identified physically only with difficulty. One would rob protein chemistry of indispensable methods were one to remove its color reactions. In the examination of natural substances they are a guide in the immense field of qualitative tests.

Likewise, in research on rubber, the question to what extent it is to be considered a homogeneous substance greatly restricts the investigator in his methods of purification. Therefore, it would be of value to him to be able to control the course of his reactions through simple color tests. Such means have been unknown in rubber chemistry.

Rubber gives almost all the color reactions of the sterols, except where its insolubility interferes. Thus, the reaction of Hesse[1] (Solution in chloroform, treatment with an equal volume of concentrated sulfuric acid; yellowish red flakes); that of Liebermann[2] (Treatment with acetic anhydride, addition of concentrated sulfuric acid drop by drop; color play, ending with dark violet blue); that of Burchard[3] (Solution in 10 cc[4] chloroform, addition of about ten drops of acetic anhydride and concentrated sulfuric acid; Bordeaux red to reddish violet color, with or without a color change); that of Tschugaeff[5] (Warming in acetic acid solution with acetyl chloride and zinc chloride; eosin-like color); that of Tschugaeff-Golodetz[6] (Solution in trichloroacetic acid, finally with the addition of a trace of formaldehyde; a deep violet color, becoming more

*Translated from the Journal für Praktische Chemie, Vol. 118, pp. 48-52 (1928), by J. P. Fahy.

intense); that of Kahlenberg[7] (Treatment of a chloroform solution with arsenic trichloride; reddish violet color), etc.

Wild Rubbers React Same as Plantation

What was true of the rubber under investigation is also true of a number of natural rubbers, "wild" as well as "plantation;" also synthetic rubber, fresh Castilloa latex[8] and latex from different varieties of Ficus, which I was able to obtain from the local botanical gardens. But it was of special value to me to be able to make experiments with rubber of the highest chemical purity thus far obtained, which I owe to the kindness of Prof. Pummerer of Erlangen.

All these samples gave the color reactions mentioned, so that there is no doubt—particularly with regard to their positive results in the case of synthetic rubber—that the colors are to be ascribed to pure rubber, and not to some by-product or decomposition product.

Without going into detail, it may be first of all stressed that the color tests are visible only with very light samples; with dark samples they are for the most part recognizable only in very strong sunlight. Among the reactions cited, two claim special consideration:

1. That of Burchard: $CHCl_3$-solution, addition of $(CH_3CO)_2O+H_2SO_4$.
2. That of Tschugaeff-Golodetz: CCl_3COOH $(+CH_2O)$

1. The Burchard reaction has shown itself extraordinarily sensitive to the quality and purity of the rubber, so that one can almost say that each kind of rubber shows a characteristic color. The best natural rubber, as well as the best synthetic rubber (polymerised by heat) gives the reaction most beautifully and clearly. On the other hand, the varieties purified by Pummerer by treatment with alkali differ from those not thus purified in that they give a Bordeaux red color and precipitates which are stable for a relatively long time, with no subsequent color changes. It may be that the color change is the result of the oxidation of rubber or of oxidation products of rubber prepared in the ordinary manner, unprotected from the air. I draw this conclusion from the fact that amyrins, which are often present in natural rubber, give, as does "Pummerer rubber," a purple color with acetic anhydride and sulfuric acid, without a color change.[9] However, the addition of a particle of benzoyl peroxide is followed by a beautiful transition through deep violet and blue to green. To be sure, in the case of "Pummerer-rubber," the addition of benzoyl peroxide does not bring about such a change—apparently benzoyl peroxide does not oxidize rubber immediately—which merely signifies that the types of rubber that give the color change already contain resinous oxidation products.

Sodium Rubber Reacts Differently

It is interesting that, inasmuch as sodium-rubber fails completely to behave as "normal" rubber in the Burchard-Liebermann reaction, the brownish yellow color which appears cannot be regarded as a typical reaction. Likewise in the case of a few low grade natural rubbers similar unexplanable phenomena appear.

2. From a quite different point of view, the Tschugaeff-Golodetz reaction is worthy of note, because in this case it is possible

to explain the nature of this color. The trichloroacetic acid which gives the violet color in this case is, to be sure, a rather strong organic acid, but is not to be compared with concentrated sulfuric acid and similar strong inorganic substances which are utilized in the other reactions. The color is due to the acid nature of the trichloroacetic acid (cf. Note 6); it disappears on diluting with water, and the rubber which is precipitated appears completely unchanged. What is more natural than to think of a halochrome? Reasoning by analogy, the latter would depend on the unsaturated character of the rubber. Hydrogenated rubber, which, unfortunately, is not at my disposal, would not necessarily give the color, if it no longer contained unsaturated bonds.

Such color reactions have never been noticed with acyclic unsaturated hydrocarbons, and accordingly sterol tests are not given by sirupy isoprene polymerized in the cold and isoprene dicarboxylic acid ester[10] polymerized by light, which, I think, are acyclic. On the other hand, one often finds in the literature the remark that diolefinic hydrocyclic hydrocarbons give colors with acetic acid or acetic anhydride with or without concentrated sulfuric acid (Wallach reaction). Moreover, sterols, amyrins and resins which give color tests are considered to have a cyclic structure. Presumably unsaturated polycyclic alcohols which also give color reactions are changed under the dehydrating effect of the reagent to diolefins. Therefore, does not this property of rubber argue in favor of a cyclic structure in the sense of the old Harries' theory?

Another characteristic, which is concerned not so much with the cyclic structure as with the unsaturated nature of rubber, is its ability, also disclosed by Pummerer and Pahl[11], of adding tetranitromethane. In this connection, I may mention that I have made the similar observation that rubber also unites with stannic chloride, whereupon it separates out from chloroform solution as a saffron-yellow precipitate. Further investigation of this substance must be discontinued for other reasons.

In conclusion, it may be mentioned that gutta percha gives colorations similar to those given by rubber.

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1. *Ann.* **192**, 178 (1878); **211**, 283 (1882).
2. *Ber.* **18**, 1804 (1885).
3. *Chem. Zentr.*, **1890**, I, 25.
4. Presumably half the old quantity to restrain spontaneous heating.
5. *Chem. Ztg.*, **1900**, I, 472.
6. *Chem. Ztg.*, **1908**, 160. Rubber dissolves in fused trichloroacetic acid (m. p. 55°). This is the more striking, as it is not noticeably dissolved by acetic acid, or mono- or dichloroacetic acid That the $-CCl_3$ group, as in chloroform, is responsible, follows from the fact that other compounds with this group show a tendency to dissolve or disperse rubber. This is true of trichloroethyl alcohol, and especially anhydrous chloral. However, trichloroacetic acid alone of all these substances gives the color, which, according to Golodetz, is quickly developed by traces of formaldehyde.
7. *Chem. Zentr.*, **1922**, II, 382.
8. Castilloa-latex behaves irregularly in giving with Burchard's reagent an intense green fluorescence, probably because of the presence of an impurity (cf. Weber, *Ber.* **36**, 3108, 1903).
9. Ultée, *Chem. Zentr.*, **1912**, II, 1469; **1916**, 1, 1251. It is possible to distinguish amyrins from rubber by the Burchard reaction, which is given by the former, but hardly or not at all by the latter. Vice versa, in the Liebermann reaction, amyrins immediately give an intense purple color, while rubber, because of its insolubility in acetic anhydride, gives a color only very gradually and hardly noticeably. Likewise, the Hesse test makes a distinction possible. If one pours the yellowish red solution obtained with amyrins into a shallow porcelain vessel, violet red rings appear immediately. With rubber this is not the case.
10. Pauly and Will, *Ann.* **416**, 9 (1916).
11. *Ber.* **60**, 2159 (1927).

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Factors in Supply and Use of Cooling Water

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THE GOODYEAR TIRE & RUBBER CO., AKRON, OHIO

WE OF the rubber industry are naturally interested in water mainly as a cooling agent. We are concerned with its source, the quantities regularly available and the temperature at which it is supplied.

A reference to the requirements of the Goodyear factories in Akron indicates how important a factor it is. The two plants must be supplied with over 20,000,000 gallons of water per day exclusive of the amount taken from the city mains for special purposes. Approximately 13,250,000 gallons of this volume are used for cooling mills, internal mixers, calendars and tubing machines. The greater proportion of this is recovered and with the addition of fresh water is employed for cooling heaters, in the reclaiming plant and for various services throughout the factories. When the day's cycle has been completed, more than 13,000,000 gallons of warm water are returned to their principal source, the Little Cuyahoga River.

In the cooler seasons all of the 13,250,000 gallons of cooling water come from the impounded waters of the river, which is fed largely by Wingfoot Lake and partly by Springfield Lake. During the summer the daily supply is a mixture of deep well water and the necessary balance from the river.

Temperature of Supply Water

The temperature of the river water averages 46° F. in winter and 70° F. in the warm season. The summer mixture of 53° F. well water and of river water has a mean temperature of 64° F. Although two small refrigeration plants furnish 50° water for special mixing units, general refrigeration has not been resorted to. In the processes of

plasticizing crude rubber and mixing rubber compounds water is needed for removing over 1,200,000 B.T.U. per minute. If the necessary amount of water were refrigerated during the summer to 50° F., there would be required a plant with a capacity rating of nearly 3,000 tons of ice per day.

When we watch an 84-inch mill mixing a batch of rubber stock, we remember that, under normal conditions, and neglecting the effect of water velocities, it has a theoretical heat transfer capacity of about 320,000 B.T.U. per hour, if the inside walls of the mill rolls are clean. We know that, with 50° F. water introduced into the rolls at a total rate of 25 to 30 gallons a minute, the average mill is actually removing heat from the stock at a rate approximating 180,000 B.T.U. per hour. Sometimes the water may carry considerable foreign matter and regardless of screening devices the spray pipes in the rolls may finally become plugged. When the proper inflow or distribution of water ceases for any reason, the mill becomes overheated, of course; and the temperature of the rolls increases still more because the walls are not kept clean. A thin film of foreign matter over the inside of a roll will decrease its heat removing capacity to a surprising degree. Special precautions for providing clean water and means of maintaining clean surfaces are profitable.

Effective Cooling Water Velocities

The factor of effective cooling water velocities in mill and calendar rolls, as well as the influence of the inside surface conditions, is often neglected. We know that by increasing the velocity of cooling water the same results can be accomplished with less water at a given temperature or with water at higher temperatures. For example the water is usually introduced into the core of an 84″ mill roll by a 1-inch pipe which has small holes or jets in the upper side. If there is no back pressure in the outlet line, the core will be half full of water. Therefore, it is possible to obtain a spraying effect on about half of the surface.

Consider an 84″ mill with rolls 26 inches and 22.2 inches in diameter respectively and with walls 5 inches thick. With 30 gallons of water per minute introduced into the two rolls by such spray pipes there results a stream velocity of 20 feet per second with a consequently great increase in cooling effect, provided that velocity continues until the water strikes the walls of the rolls. However, if there is sufficient back pressure in the effluent lines to raise the level of the water so that the spraying action becomes inoperative, the effective velocity is merely the resultant of that due to the axial and transverse flow through the rolls. Then the velocity will be around one foot per second so that the

cooling effect will be greatly diminished. The same condition is true when the jets of water are directed downward through the body of water in the lower half of a roll. Obviously, any system which does not allow taking advantage of high water velocities is incorrect in principle. Insurance of the most efficient results suggests water outlets of ample size to make back pressure impossible. An open, gravity outflow is preferable.

Recirculation in connection with high velocity offers a means of conserving water whenever a scarcity justifies the expense. Again, this allows the use of less water or water at higher temperatures. For instance, tripling the velocity of 50° F. water permits a reduction in its volume by one third, or the original amount at about 75° F. will provide the same cooling. Of course, recirculation is always a part of a refrigerating system.

The next improvement in milling, and possibly in calendering processes, will no doubt be the use of hardened steel rolls. Mill rolls can now be made with walls not over 2 inches thick and with surfaces hardened to the same degree as are those of the ordinary cast iron rolls with their 5-inch walls. The thinner-walled steel roll has three times the heat conduction capacity. With proper provision for cooling water contact there can be obtained an increase in milling efficiencies and a considerable saving in water. Temperatures can be more easily controlled due to the shorter "lag" through the walls. The steel-walled roll is not quite out of the development stage and its cost is too high now. But it will no doubt be available soon at a reasonable ultimate cost. The method of construction will apparently consist in welding or shrinking steel shells on cast steel journals with a supporting core inside the shells.

An adequate supply of cold water at a constant pressure provides many obvious and desirable features. It suggests refrigeration whenever that is the only recourse. Uniform temperatures in the preparatory processes mean more equable stock conditions. Heaters can be cooled uniformly, thus eliminating any variations in vulcanization that may arise as a result of cooling irregularities. Finally, only when sufficient cooling water is assured at all times is it possible to take the next progressive step in plasticizing, mixing, calendering and tubing operations—that is, automatic temperature control.

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Sources and Application of Cooling Water

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IN the Firestone plants, the application of water for cooling purpose has progressed from year to year along the following lines.

The original installation of mill rolls included a stuffing box in one end of the roll, with two 1½" holes in the end of this stationary box, one being the water inlet with a 1" perforated standard pipe extending across the entire length of the inside of the roll. The cooling water filled the entire cavity of the roll, placing it under line pressure with a drain through a 1" pipe to the other connection in the stationary stuffing box. This water is returned to a common header system and finds its way into the storm sewer system.

This method of mill roll cooling required approximately 40 gallons of water per mill per minute, the water entering the roll at a temperature of 56 degrees and leaving at approximately 60 degrees, or a temperature rise of only 4 degrees F. With this method, the difference between the temperature of the outgoing water and the stock was 85 degrees. This method was exceedingly inefficient and used a large quantity of this scarce well water.

Several years later it became necessary that more efficient means be found for cooling mill rolls. At that time the engineers designed an aluminum fin vane that extended the entire length of the inside roll cavity with a tip that forced the water directly against the inside surface of the steel roll. This aluminum vane also acted as a paddle which kept the water agitated as the roll revolved, and coming more rapidly in contact with the roll surfaces.

The same type of stuffing box and connections in the neck of the roll were used with this method as with the original method, which meant that the roll was entirely filled with water. Improvements, however, were quite appreciable, showing a decrease of approximately 50% in water consumption and a temperature rise of 100%. The temperature difference between the stock and the outgoing water in this case was from 77 to 81 degrees F.

The Engineering Department, being encouraged by these

results, during the following year decided that still more efficient means of cooling could be found. Consequently, it was decided to make further research in this direction. This time quite a radical departure was made from the original type of cooling. The solid stuffing boxes were removed from the ends of the roll necks and the connection left entirely open, so that the water in the roll cavity was only a few inches and filled that area which constituted the difference in diameter between the cavity and the neck opening. This allowed the operator at all times to readily take the temperature and see the amount of water he was consuming in the roll.

The second step with the new method of roll cooling was the removing of the aluminum valve from the water inlet pipe and the inserting a new type of feed pipe into the roll cavity.

This method of admitting the water to the roll formed a very fine mist constantly against the roll surfaces which was rapidly replaced by fresh water, allowing the heat to be carried away from the roll surfaces very rapidly by the constant changing of the small quantities of water.

Each of these steps began to show improvement, but there was one difficulty which we found existed inside the roll after a month's usage of water in this manner. A thin film of gummy rusty scale stuck to the inside of the roll surfaces which had an insulation value equal to approximately 4" of iron. It became necessary then to keep this filmy scale removed. This was accomplished by inserting in the cavity of the roll, foundry cleaning stars made of white iron, chilled through to a glass hardness. As the roll rotated, these stars tumbling over each other very adequately kept the roll surfaces commercially clean.

The final results of this type of roll cooling show a decrease in water consumption of another 50% and a temperature rise of the water inlet to water outlet 75 to 100% more than the second vane method. The temperature difference at the maximum efficiency was only 45 degrees between the stock temperature and the temperature of the outgoing water.

This, we found, is as efficient a job as can be done with the present type of roll construction. If the outgoing water is higher than 90 degrees F., then the stock temperature goes up to a point where it is dangerous to some particular compounds.

However, it is a continuous research problem to keep up with the chemist and his peculiar and ticklish stocks, so from year to year probably other steps and more efficient means of removing heat from stocks will be developed. Such methods may be along lines of roll design and may be some method of surface roll cooling by means of rapid evaporation.

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Chilled Iron Rolls in the Rubber Industry

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PROBABLY no single part of a machine is more vital to the manufacture of rubber products than the chilled iron roll. It is used in most operations from the cracking and washing of the crude rubber to the final accurate calendering where the variation is limited to fractional thousandths.

As you gentlemen are familiar with the history and development of the rubber industry, it is not necessary to go into any details connected therewith, but it might be well to recall to your mind the fact that the vulcanizing of rubber was developed in the year 1844 at Naugatuck, Connecticut, a town located about ten miles from Ansonia, where Farrel Foundry and Machine Company was started in 1848.

The discovery of the vulcanizing process made possible the practical use of rubber, and manufacturing of the product on a small basis very soon started, developing into one of the largest industries of the United States.

In Mr. Farrel's diary of 1854 there is an entry regarding his negotiations with a Mr. Goodyear of Naugatuck, and finally the memorandum of agreement of sale of a three-roll 20x48" calender for $2,400 and a four-roll 20 x 48" calender for $3,400. The calenders were designed and built but the chilled iron rolls had to be imported from England. There were already some mills in this country which had imported chilled iron rolls for rolling copper and brass products and for calendering paper.

The initiation of the rubber industry caused Mr. Farrel to decide to start the production of chilled iron rolls and there is a notation in his diary dated 1854 describing the first calender built for Goodyear and expressing the desirability of in future making chilled rolls for the fast developing rubber trade, rolling mills and paper machinery. Since that time for nearly seventy-five years Farrel Foundry and Machine Company and the Birmingham Iron Foundry (now combined) have endeavored to build machinery and chilled iron rolls which would meet the requirements of the rubber industry and, through improvements in these machines, permit the speeding up of production until it has reached the remarkable output now existing in Akron and elsewhere.

Unfortunately, the builder of the machinery cannot be as familiar with all of the difficulties that develop as is the user. It is, therefore, most important for both the user and supplier to have frequent interviews and to discuss thoroughly their respective difficulties. This condition is particularly true in connection with chilled iron rolls as rolls for different purposes are made in different ways, and if the supplier is acquainted with the manufacturer's troubles he can very often make changes which will result in giving better service. On the other hand, the user should understand the difficulties surrounding the manufacture of the rolls and should take precautions to use the material in a manner which will lessen the possibility of breakage and resulting complaints.

Insofar as the rubber trade is concerned, rolls are divided into four principal classifications: First, crackers and washers; second, refiners; third, mill rolls; fourth, calenders. Each of the above classes of rolls vary, both in regard to their chemical analysis, and to their physical qualities. Before speaking of the special peculiarities of these rolls it would be well to set forth the method of molding and casting chilled iron.

Chilled roll iron may contain a carbon running anywhere from 3.00 to 3.75%, depending on the physical characteristics desired in the roll. By the proper adjustment of the silicon, sulphur, phosphorus, and manganese, together with the cooling speed, the carbon may be retained entirely as combined carbon, resulting in white iron, or only partially as combined carbon, resulting in either mottled or gray iron. A combination of the above structural characteristics is present in most chilled iron rolls.

How the Body of the Roll is Formed

The body of the roll is formed by a heavy cast iron chiller, and the necks by sand molds. The difference between the heat conductivity of the iron chill and the sand mold results in the barrel of the roll, where the molten iron comes in contact with the chiller, having a white iron skin, of varying depths, depending on analysis and purpose, the necks being gray. Under the microscope, the white iron portion of the roll would show a structure composed of cementite and pearlite, the gray part of the roll a structure of pearlite and graphite. From this it will be seen that quick cooling gives a hard surface, for instance, cementite, but where the roll cools more slowly the cementite is changed to free graphite which is comparatively soft.

Between the zone which consists of cementite and pearlite, and that consisting of graphite and pearlite, there is an intermediary zone

which has both cementite and graphite—in other words, is composed of what is known as mixed iron. A clear chill is of the same hardness and usefulness until the point of mixed iron is reached. At that point the soft iron, or graphite, will show up in the form of minute specks on a polished surface.

One of the great difficulties is to control the various elements in the roll and the temperature of pouring so as to give a chill of the correct depth. Chilled iron is very brittle and the strength of the roll is principally in the backing iron or in the zone consisting of graphite and pearlite. The chilled surface must be sufficiently deep to resist the crushing or abrasive stresses and yet not so deep as to detract from the strength which is expected to be found in the softer iron which lies below it. As will be shown later, this depth of chill varies for different types of rolls.

The roll is cast on end and bottom poured. This is accomplished by runner gates leading to the bottom part of the roll casting—for instance, into the journal or gear fit. The iron is poured from the ladle into pouring boxes on top of the runner gates which lead the iron into the roll at a tangent, setting up a swirling motion of the iron as it rises through the body of the roll. This swirling motion tends to throw any slag or foreign particles toward the center, leaving the outer surface comparatively free from defects. The pouring is done very rapidly, and continued until the iron overflows at the top end of the casting. The iron molds are carefully coated with a lead wash to prevent the molten iron burning onto the mold itself, and all sand parts, for instance, cores and necks, are washed with graphite to prevent any sand slag on the surfaces.

The Question of Shrinkage

The chilled part of the roll sets up in a very few seconds and the shrinkage in the interior of the roll is fed from a riser at the top of the casting. This question of shrinkage is one of the first difficulties to be overcome. As mentioned above, the skin of the roll sets up almost immediately and this skin is of chilled iron. Chilled iron shrinks about ¼" to the foot, whereas the softer iron shrinks ⅛" to the foot. This difference of two to one causes the outer shell to exert a crushing stress on the interior, putting the chilled shell itself in tension. If the temperature of pouring varies slightly from that desired, or if the chemical composition of the roll is off a very small amount, the roll may split from one end to the other when it is removed from the mold. Another danger in the casting is the tearing of the body from the neck, this also being due to the difference in the coefficient of expansion of the chilled iron from that of the unchilled iron.

The majority of rubber rolls are cast with a core. The placing of a core in a gray iron casting is not difficult as chaplets are used to hold the core in exact position to prevent its floating or moving out of place when the casting is poured. These chaplets fuse into the iron and in no way affect its strength. The problem of the chilled iron roll is quite different. Any chaplet that might be placed in the body of the roll would immediaely show up when the roll was machined. The chaplet does not fuse into or become part of chilled iron and it cannot be used where a clean chilled iron surface is required.

It is, therefore, necessary to support the core at the bottom end and to again hold it with chaplets at the very top in the part of the

casting which constitutes the riser and which is later cut off. If the roll is short this is not such a serious problem, but on long rolls, such as 84" mill rolls, there is great possibility of the core buckling with the result that the thickness of the wall of the roll is not the same all the way around. Many of you have probably seen mill rolls which have broken and showed the core somewhat out of center, and have probably remarked upon the inefficiency of the foundry which made the casting. Every effort is made to keep these cores central and it is hoped that the next time you have occasion to see a roll broken, with a core slightly off center that you will appreciate the difficulties connected with the casting and be as generous as possible with the roll maker.

Washer and Cracker Rolls

The washer and cracker rolls are usually subjected to heavy pressures and considerable wear. In order to permit recorrugating, it is necessary to chill these rolls more deeply than is the case with other types. Chilled iron has very little strength and if the chill is too deep there is danger of the roll breaking. It is quite difficult to obtain a deep chill and control it with any degree of accuracy. A slight variation in casting conditions may make the chill shoot well into the center, with the result that the roll must be scrapped. Forunately, the cracker roll is seldom subjected to severe strains of expansion and contraction and therefore has to withstand only the stresses of its actual work.

The problem facing the manufacturer is to get a proper depth of chill for the type of cut used, and a strong hard iron which will resist wear and breakage of the teeth. Breakage can be reduced by using the correct cut for the particular duty which the roll is to perform and taking precautions to prevent the cut part of the rolls coming in metallic contact with each other. The question of neck size is important. Records show that much of the breakage is at the neck close to the body. In old crackers the necks are probably too small for the work now being done. In new designs larger fillets are placed between neck and shoulder and the necks increased to give strength in proportion to the body.

Refiner Rolls

The refiner roll probably has the hardest treatment of any type. The rolls are run together with considerable friction and are set up with great pressure. The friction on the surface causes excessive heat and to carry off this heat cold water is run through the core. There is much breakage in this type of roll and records show that about 85% of the breakage occurs in the large size roll, whereas, in the case of 30" refiners, this roll is twice as strong as the smaller roll. This clearly shows that the breakage in refiners is not due to a weakness in design, or in the iron, as the small roll is subjected to just as much pressure as the large one and yet in the majority of cases does not break. Practically all breakage of refiners is in the form of longitudinal splits. If the breakage were due to working stresses in excess of the strength of the material, the fracture would be circumferential, although heat strains also enter into such breakages.

The writer believes that the breakage of these rolls is principally due to expansion and contraction, and the greater the diameter of

the roll, the greater the stresses that are set up due to the difference in expansion between the chilled iron on the exterior and the softer iron center.

If a refiner is started, by warming up the interior with steam, and later when the temperature of the surface gets to working heat, cold water is admitted, there is a sudden change in temperature which sets up a strain in the core and is very liable to start a crack. Furthermore, the interior of the roll is in a strained condition due to the fact that the exterior has hardened first and the interior is compressed by the surface. Irrespective as to whether the warming up is external or internal, considerable time should be used in the operation. This feature has been carefully studied in metal rolling mills and the writer recently read a German treatise on rolling mill practice in which it was stated that the warming up of rolls should require eight hours and the process should be accomplished by using water at a temperature of about 175° F. Needless to say, our present production methods would not tolerate such delays.

Breakage From Expansion and Contraction

Breakages from expansion and contraction are not limited to the longitudinal position. Let us assume a roll is twice as hot on the exterior as on the interior. The chilled shell, already under severe tension from its casting condition and with double the coefficient of expansion of the core, expands lengthwise four times as fast as the core. This causes the chill to have a stress tending to pull it apart and tear it away from the softer interior. The hottest part of the roll is probably the middle and this expansion strain combines with the working stress to cause circumferential breakage. This condition is even more applicable to the mill roll than the refiner.

There seems to be no standard practice in regard to the crowning of refiners. We have cases where we have crowned 21 and 24x32" refiners as much as fifteen thousandths total, whereas other customers do not wish more than one-third of that amount. Of course, the greater the crown the more pressure can be applied to the rolls without causing them to open in the middle, but, on the other hand, this great pressure is subjecting the outer layers of the metal to considerable flexing on each revolution. Chilled iron is very brittle and cannot stand the continual flexing without breaking through fatigue.

If the rolls are set up with the great pressure and have not enough crown on them the result is that the rolls bear heavily on the ends and open up in the middle and it is quite possible that small pieces will break off the end of the roll and that this chipping, or spalling, may then develop into a crack.

With a view of reducing the amount of breakage in refiner rolls, we have tried making them of a comparatively thin shell, for instance, three and one-half to four inches. Theoretically, the thinner the shell the less danger there should be from splitting in so far as the effect of expansion and contraction is concerned. This is clearly shown by pouring hot water into a thick glass and a thin test tube. The thick glass is very liable to crack, whereas the thin test tube used in the chemical laboratory can take boiling liquids and practically never break. We have found that the thin shell refiner stands up better than the thick shell unless the roll is subjected to great pressure. If, as we have known cases, the rolls are set together cold with a ten-foot bar on the setting up screw, and then steam is turned

on them to bring them up to working temperature, it is quite probable that the thin wall may tend to break down. The larger roll has a flatter arc than the smaller roll and therefore cannot withstand the pressure on the arch of its surface as well as the smaller roll with the result that a longitudinal crack may develop.

For information purposes we have broken up many of these split rolls and the fracture shows that the cracks usually start on the inside surface and work towards the exterior. Just how long it takes such a crack to develop we do not know, but from the appearance of the fracture it is slowly progressive and a refiner roll may hold together for several days or weeks when the crack has nearly reached the chilled surface. Sometimes a spall or flaking of the hard metal will occur at the point where the crack passes through the chill. We know of several cases where spalls have been brought to our attention as an evidence of weakness but when the roll was broken the crack was seen going from the interior to the point where the spall occurred.

Mill Rolls

The mill roll is probably worked nearer to its designed strength than any other type. The strains are not as severe as in the refiner roll due to the fact that there is not the variation in temperature and the rolls are not set up with such pressure. However, they are much longer in proportion to their diameter and the 22x84" mill roll has less factor of safety than any other size. Practically all breakage of mill rolls is circumferential, which clearly indicates that the breakage is due to heavy working stresses added to the condition of hot surface and cool core. Exceptionally tough or cold stock or improper feeding into the mill may be the direct cause of breakage. Mill rolls are made of strong iron and the chill is kept much lighter than in other rolls. As stated above, the chill has very little strength and as mill rolls have relatively thin walls, the depth of chill is kept at approximately five-eighths to three-quarters of an inch.

One of the greatest problems facing the milling operation is the cooling of the rolls. With this necessity in mind there has been a demand for rolls with thinner shells and yet of equal or greater strength than those now in service. Many rolls with thinner walls have been tried, but it is difficult to obtain a roll with a thin wall and yet of sufficient surface hardness. Chilled iron resists abrasion better than any other material but chilled iron has not the strength of steel. Farrel-Birmingham Company has recently developed an alloy roll which will give the same strength as the usual type of chilled roll, with about 25% less wall thickness, and are developing a mixture which gives prospects of permitting even thinner walls with the same strength roll, or conversely will give a stronger roll if walls are not further reduced.

Unfortunately the manufacturer of the roll is not in a position to try out all of the theories in regard to cooling, but a theoretical investigation leads us to believe that the question of wall thickness is not as vital as certain other factors. Professor Joseph W. Richards, who had the chair of metallurgy at Lehigh University, states in his volume on "Metallurgical Calculations" as follows: "The valuable practical conclusion is, that the thermal resistance of the walls of the pipe is insignificant as compared with the whole thermal resistance, and the thickening or thinning of the walls of

the pipe, or the substitution of copper for iron because of its greater thermal conductivity, is practically unnecessary for thermal considerations, since such can be expected to make practically no change in the thermal resistance of the whole system."

High Thermal Resistance of Scale

The above quotation refers to the transfer of heat from fuel, to a liquid inside of a pipe, but is entirely comparable to the case of a roll where the hot material is the rubber surrounding the roll and the material to be heated is the water on the inside. Professor Richards says in the same volume that scale two-tenths of an inch thick on the surface of the pipe would have a thermal resistance one hundred eight times that of iron. Or, in other words, scale two-tenths of an inch thick would have the same resistance to conductivity as 21.6 inches of iron. If these figures are correct—and they are quoted from the highest authority on this subject—it would lead one to believe that the difficulty in cooling compound on mill rolls is primarily due to scale or mud which accumulates on the interior of the roll, causing the thermal resistance from roll to water and the thermal resistance of rubber to roll, to be of much more importance than a variation in thickness of roll wall. This condition is thoroughly recognized in marine water tube boilers where there is always danger of salinity in the feed water. If such tubes are not cleaned at the proper intervals there is great danger of their being burned through, due to the fact that the heat of the gases is not conducted through to the water with sufficient rapidity. Hence, the pipes are not kept below the melting point.

The average well water may be high in lime or magnesium, either of which elements will give a heavy scale, and if river water is used there is apt to be mud and slime deposited unless the water is put through a filtration plant. There is absolutely no scale on the interior of the roll after the core is removed. In place of scale there is a hard skin of iron due to a very slight chilling effect when the iron comes in contact with the core, but this iron is an integral part of the roll and its conductivity can be treated as that of hard iron which is given by Professor Richards as the same as for hard steel. The core is covered with a lead or carbon wash and this wash keeps the interior of the roll entirely free from any scale or slag, as carbon fuses at a temperature higher than 3000 F., whereas the roll is poured at a temperature of approximately 1000 degrees below that point.

Methods of Applying Cooling Water

Next important to the condition of scale is the method of applying the cooling water. Many rubber mills complain of the large volume of water used in cooling. The larger the core in the roll the more water it requires to fill it, but it is believed that having the core full of water is the wrong system. The only water that does any good for cooling is the thin film which comes in actual contact with the metal. This film should be constantly changing and the best way to accomplish such results is to use a spray pipe which directs a strong spray of water upwards against the interior of the wall. Unless there is free drainage from the body of the roll the spray pipe will be covered with water and be of absolutely no value in so far as delivering a spray is concerned. If the spray

is applied against the interior of the roll with considerable force, it will tend to remove any globules of water that may cling to the somewhat roughened surface of the interior, and this constant changing of such film of water will carry away heat very rapidly. If this spray is applied as described above, the roughness of the surface will be of some advantage, the same as the veins on an air cooled engine against which there is a constant flow of air.

If the data available on thermal resistance and conductivity is correct, it would seem that the best results could be obtained as follows:

First: By using jackstones or some such rough pieces inside of the core which would tend to dislodge or wear away any scale or mud which might tend to accumulate from the circulating water.

Second: By permitting a sufficiently free drainage to carry off all surplus water.

Third: By locating the spray pipe so that it will be above the level of the water which is being drained off, and deliver a flow of water against the roll shell.

Freedom From Scale Important

Based on Professor Richards' theory, no great advantage is obtained from the thin wall roll provided the interior surface is clean, but the increase in diameter of the core gives a greater cooling area. This area of inner wall increases directly as the increase in diameter of the core. As an example, if we compare two 22x84″ mill rolls —one with a 5″ wall and the other with a 3″ wall—the cooling area is as 3 is to 4 or, in other words, there is 33⅓% more cooling area in the case of the thinner shelled wall and it is believed that this factor is of more importance than the resistivity of the iron.

We recently made a line of 60″ mills, some of which were furnished with rolls of 3″ wall and others of 4″ wall. If the question of area of internal wall is taken into consideration, there should be a difference in cooling effect of approximately 15% in favor of the thin walled rolls. We have recently had a report giving the temperatures, and the thin walled rolls had surface temperatures varying from 10% to 14% less than the temperatures of the thicker walls, which is surprisingly close to the calculations made on the basis of area only. This test can be considered a proper comparison as all of the rolls tested were new. It is not believed that a test is of any great value in which new rolls are compared with old ones, as it is highly probable that the old rolls have a coating of scale on the inner wall.

Calculations made from certain tests on an 84″ mill showed that the total thermal resistance between rubber compound and water on a roll with a 4½″ wall was divided approximately as follows:

Thermal resistance rubber to roll	41%
Thermal resistance through roll	30%
Thermal resistance roll to water.....	29%

In this case the interior of the roll had been cleaned and was free from any scale deposit from the water. If this roll wall had been reduced in thickness by 33⅓%, or made 3″ thick, the total difference in resistivity from compound to water would have been less than 12%, or would have amounted to only 3 degrees reduction in

stock temperature. These calculations do not take into account the increased area of the larger core which had been discussed in a previous paragraph.

All of the above discussion is based on the present method of cooling—for instance, taking off the heat generated in mixing and compounding rubber by passing the heat through metal and in turn cooling the metal by means of water. Is it not possible to accomplish the cooling of this rubber in a more direct and possibly simpler manner? In certain other industries the surface of rolls becomes excessively hot and is cooled by an air blast blowing directly on the surface. An air blast in the case of mixing rolls would be detrimental unless it could be so applied as to prevent the danger of blowing the pigments or compounding powders away from the rubber. Could not this be done by making a three roll arrangement by means of which the rubber can receive greater cooling by means of air and at the same time an air blast be used on the surface of the rolls without danger of blowing away any of the ingredients?

Calender Rolls

The roll which requires the greatest accuracy is the calender roll. This roll is subjected to pressures not as great but somewhat similar to those encountered in the case of the refiner roll, but at the same time is subjected to alternate heatings and coolings due to the accurate temperature control required on the surface, and furthermore, must have an even line of contact with its neighbor under the conditions of heating and cooling and under the particular pressure for which it is designed. A roll that is cored will be sufficiently strong but if the wall is somewhat thicker on one side than the other or if there is a very slight porosity in the neighborhood of the core, the roll will not expand evenly when heated. It may be ground perfectly round when cold but when heated it will become eccentric. For this reason all calender rolls are bored. They are usually cast with a core and then bored out to a diameter about 3″ larger than the diameter of the core. This gives a true hole through the roll and removes any porous metal which might be in the center of the casting. It is probable that expansion and contraction is largely responsible for the breakage of calender rolls and it has been found that they are subjected to the same stresses in this respect as are refiners.

When a calender is started after a shutdown, care should be taken that it is turning over before steam is turned on the rolls as otherwise it is very probable that a break or split will take place along the line somewhat below the level of the drain. After the roll is stopped, the steam which has been in it condenses and the lower part of the roll becomes filled with water. Water is a perfect insulator and when steam is turned on, and the roll remains at rest, only the top part of the roll expands and breaking stresses are set up at the water line. It is sometimes difficult to establish this maltreatment of the roll as a cause of breakage due to the fact that the crack does not always come directly through the shell at the time the trouble starts.

Great care should be taken in connection with controlling the surface temperature. A 24x66″ calender has a wall thickness of from 5 to 6″ and it takes a reasonable time for the heat to pass through it. It may happen that steam has been on the rolls and they are suddenly found to be too hot on the surface. The steam is cut off

and as the cooling does not take place quickly cold wa[illegible] is [illegible] mitted to the interior. This puts a sudden strain on the interna[illegible] surface changing it from the high temperature due to steam t[illegible] the low temperature due to cold water, and it is not strange that the crack starts. If precautions could be taken to prevent admitting a large amount of cold water in the body of the roll it is quite probable that its life would be materially increased.

The greatest number of breakages on calender rolls in proportion to the numbers in use takes place on the 32" diameter. These rolls are fully as strong as the 24x66" type in so far as engineering calculations are concerned. The iron used in them is of the best and the fact that they break more often than other sizes must be due to other causes than weakness of material. We have previously mentioned in this paper that it is the larger refiner roll that breaks in place of the small one and we believe that the cause of breakage of the 32" calender is due to the fact that its larger diameter means more expansion and contraction under the variations in temperature. We might mention here that this is no argument against the large size mill roll as the mill roll is continually cooled and not subjected to constant alterations of heat and cold. As a proof of the fact that the working stress on these large size calenders is not the cause of the break, I would cite a recent instance in which a 32x92" roll was cracked for two-thirds of its circumference but nevertheless operated without further breakage. It was finally removed from the calender and broken by dropping one end. If the roll were to break from working stresses it would probably have broken in two parts rather than cracking and remaining in operation with only one-third of its holding surface left.

Machining of Chilled Iron

The machining of chilled iron requires special machine tools. The iron is of a scleroscope hardness of approximately 70 and can only be cut very slowly. The usual method is to use a broad faced scraper tool which takes off the surface in the form of small shavings which look like needles. The cutting is accomplished at a speed of about 16" per minute and the cut is only a few thousandths deep. Many types of tool steel have been tried but the machining of chilled iron is not a question of the tool standing up under the frictional heat of cutting, but it is a case of its maintaining its hardness against a very hard surface. Many of the best cutting high speed steels break off their edges when used against chilled iron.

The most important factor in the calender roll is the accuracy of grinding. Each type of work to which a calender is subjected has its own peculiar requirements and a calender that is ground for sheeting out one type of rubber cannot be expected to do good work on friction or skim coating. It is possible to so grind a calender as to give compromise results but perfection is not usually obtained on various types of work with the same machine. Rolls are ground so as to permit a perfect line of contact between the top and middle and the middle and bottom when running the particular material for which the calender is designed. For average work the middle roll is straight, the top roll crowned, and the bottom roll concaved. The crowning of the top roll compensates for the bending of that roll when a bank of rubber is run between it and the middle roll, the result being an even calendering of the material which passes between these two rolls. The pressure at that point has not only

straightened out the top roll but has bent the middle roll down a few thousandths. The operation between the middle and bottom roll is not quite sufficient to straighten out the middle roll from the pressure on its under side, therefore, a slight concavity on the bottom roll is necessary in order to give an even gauge between the bottom and next to bottom rolls.

These calender rolls are ground running on their own journals (not on centers) and therefore, there is no chance of the face being out of round with the necks. An accurate caliper which is self-recording measures the curvature of these rolls and this curvature —either crowning or concaving—is applied by means of a device on a grinder which we have built for that special purpose. The maximum difference in diameter between the middle and the end of the roll is not the only important factor. In the case of calender rolls the grinding is done with the roll cold and then while it is still turning it is heated with steam and a dial indicator run on the surface to make sure that it expands evenly. If there is the least unevenness of expansion the roll may be rebored until the results are correct.

Chilled iron rolls are used in many other fields besides the rubber industry, principally in steel rolling, rolling of non-ferrous metals, paper calenders, textile and special finishing calenders, rolling grains and oils, making corn flakes and other cereals, grinding paint, ink and chocolate, making soap flakes, and in fact for rolling all plastic material. We have had occasion to supply all of these fields and each one of them has its own problems some of which are more difficult to solve than those connected with your particular line.

We are sometimes called upon to make chilled iron rolls of unusual proportions. For instance, about four years ago we made for the linoleum industry a roll 72″ in diameter 90″ face. This presented a difficult engineering problem and required many special riggings. However, we made it to the satisfaction of our customer and were very much pleased to see the amazement of two Austrian manufacturers when they learned that such a roll had been made as they had been trying all over Europe, Krupp included, to get a roll of that size and were told that it was impossible.

We are now engaged in making a paper calender stack with rolls 298″ face. These rolls will be about 35 ft. long. The largest one is 36″ in diameter and will take about 110,000 pounds of metal to pour it. Not only is it a difficult problem from the viewpoint of handling the iron, molding and transporting, but when it is realized that this roll must be crowned to within a quarter of a thousandth of an inch of exact curvature, it will be appreciated that we must combine quality with quantity.

Probably the most accurate grinding on any rolls is required on these paper calenders. A stack consists of about eight to ten rolls running one on top of the other. All of the weight of the stack rests on the journals of the bottom roll and the bottom roll is so crowned as to compensate for the bending effect of the rolls above it. The 36x298″ roll will have to be crowned probably about ninety thousandths of an inch. When the rolls are ground they are placed one on top of the other and a light passed back of the line of contact. If a blue flicker can be seen between the rolls they must be reground and a blue flicker is less than a quarter of a thousandth of an inch.

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Open Mill Mixing vs. Internal Mixers

P. P. Crisp

THE MILLER RUBBER CO., AKRON, OHIO

AT the present time about 80 per cent of all the mixing at the Miller Rubber Company is done in internal mixers. All tires, tubes, heels and in fact all stocks with the exception of highly colored bath caps, water bottles and the like are mixed on these machines.

The transition from mill to internal mixer has been gradual as there were many difficulties to iron out, both in the original mixer itself as well as in the operation.

Our first experience with the internal mixer dates back to 1916 when we installed a small machine. The troubles encountered with this machine were largely due to the inability of getting rid of the heat generated during the mixing operation. In 1919 we installed the first mixer with which we mixed tire tread socks with some degree of success. Our biggest difficulty at this time was not the dispersing of the powders or pigments in order to meet gravity and tensile specifications, but was rather due to the fact that the mixed stock refused to run through the calendars and tube machines on account of being too stiff.

The next problem was then to change compounds where necessary so that the finished product would meet all specifications as regards tensile, etc., and still be soft enough to run through the ensuing operations. Until 1923 we used the type of internal mixer which handled about a 275 lb. batch. At this time we installed a mixer which would take the 775 lb. batch of a gravity of 1.2. We found that this machine was a vast improvement over our past mixing machine and showed us many advantages over the mills as

regards mixing cost, ease of quality control, low compound room cost, floor space saving and the isolation of gas black dirt.

Refrigerated Water and Internal Mixers

In the past four years we have changed a large percentage of our mixing from mills to internal mixers. A condition in our factory which helped us to a large extent in the development and use of this type of machine was the fact that we have refrigerated water which runs at an average of about 43 deg. F. the year around. There are conditions in each factory which are peculiar to that specific plant. The following comparisons between mills and internal mixers might not hold true in all rubber factories and are only given to show why we, with our existing stocks and existing factory conditions, do in a large measure mix by the internal method.

From a production cost standpoint, the internal mixer has made it possible to reduce our mill-room costs very materially. The biggest reduction in all cases was in direct labor and electric power. For comparative purposes, I will deal in these two items only, taking first an average tread stock, then a friction or coat stock and finally a heel stock. The cost per 100 lbs. and machine hour production was as follows:

On an 84 inch mill the direct labor for tread stock was 20 cents per 100 lbs. as against 12 cents on the internal mixers. The power was 29 cents as against 18 cents on the mixers, and the machine hour production was 400 lbs. as against 3,700 lbs. with the mixers.

The coat stock on the mill showed a direct labor cost of 25 cents as against 14 cents, and for power, 36 cents as against 23 cents, and machine hour production was 322 lbs. against 3,210 lbs.

The heel stock shows a direct labor of 17 cents as against 9 cents, a power charge of 24 cents as against 14 cents and a machine hour production of 450 lbs. as against 4,560 lbs.

In all cases these comparisons contain the cost of running the batch out mills and when speaking of the mixer, I am, of course, including the mills which are considered as a mixing unit. These comparisons indicate an average reduction for power and direct labor of 21 cents per 100 lbs. in favor of the internal mixer. There is also a very material reduction in cost possible in the compound room. As you can readily see, it would cost only slightly more to weigh out the ingredients for an 800 lb. batch than it would to compound a 200 lb. batch.

Better and Cheaper Supervision

The next advantage to consider is the case of supervising quality. One supervisor will supervise two mixing units capable of turning out 60,000 lbs. per shift. We test each mill batch as it comes from the batch-out mill of the mixer for gravity, cure, stretch and plasticity. If a batch is found to be defective, the supervisor can check the temperature chart on the mixer and this will tell whether the mixing crew lived up to specifications as regards time and temperature.

It is also possible by the installation of internal mixers to save much valuable floor space in the mill room. This is especially desirable where it is possible to hook up mixing equipment direct to a large producing calender or tube machine installation.

Too much stress cannot be put on the point of quality mixing of

high grade present day stocks. This is especially true of the present day balloon tire tread stock. With these particular stocks it has been necessary to work out specifications very carefully to get good dispersion. The addition of the pigments in the proper sequence, the use of the mixer weight only during a short period in the mix and the use of an additional batch-out mill are the most important points here.

We use three batch-out mills for this class of stock and after the batch is divided in three parts it is given a seven-minute mill-mixing before the batch-off operation is begun. This is as long a mixing time as the average 84 inch mill batch is given after the pigments have been added. You can readily see that this should handle our dispersion problem. Our laboratory makes special tests from time to time for dispersion and since using the above-mentioned precautions, we have had no trouble whatever.

On cheaper grade stocks such as heels, automotive accessories, cab tires, etc., the operation of the mixer is much easier than the use of mills. On very cheap batches much trouble is encountered keeping them on the mills as well as in the addition of large quantities of oil which these stocks usually contain. The internal mixer will turn out these stocks in a surprisingly short time with practically no production trouble.

The greatest trouble encountered in the use of these mixers has been the elimination of heat generated and the rapid war in the mixing chamber. The latest development in these machines has been the use of sprays in the jackets for cooling which takes away the heat faster, and in the use of inside jacket liners which are more resistful to premature wear and when they are worn out, can be replaced over the week-end at a comparatively small cost.

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Power Variables in Milling and Mixing Rubber

P. S. Shoaff

THE GOODYEAR TIRE & RUBBER CO., AKRON, OHIO

OF THE expenses involved in the milling and mixing of rubber, the costs of materials and of labor are constantly subjected to the closest analysis. Economic drives are concentrated mainly upon them. Power, being a less tangible thing, often eludes the attention that is warranted by the profitable study of factors which may introduce savings. Frequently its cost equals or exceeds that for labor in a mill-room operation. When in a large factory there may be previously plasticized daily a half million pounds of crude rubber, when a half million pounds of master-batches are prepared, and when every day one and a half million pounds of compounded rubber stocks are mixed, power bulks enormously. Milling and mixing equipment to do that demands a power input of approximately 21,500 horsepower, or about 386,000 kilowatt hours. At one cent per K. W. H., as an example, this represents a daily cost of $3,860. With an average of 250 working days a year, the total reaches nearly a million dollars. The smaller manufacturer makes a proportionate outlay for power in these preparatory processes.

So it would seem worth while to study power applications and those variables which may be turned to account in the search for greatest efficiency. Some points which may be mentioned are in part a review or confirmation of the findings of others which have appeared in published articles[1] [2], other facts are from observations of very recent practice.

Factors Governing Power Input

Neglecting machine losses, the principal factors governing the power input to the ordinary two-roll rubber mill are, first, the speed of the front roll; second, the friction ratio, *i. e.*, the ratio of the surface speeds of the two rolls; third, the gauge of the rubber

[1] H. C. Young, *India Rubber J.*, Vol. 65, No. 10, pp. 405-410 (1923).
[2] R. B. Stringfield, *Chem. and Met. Eng.*, Vol. 32, No. 2, pp. 51-54 (1925).

or the stock, and, fourth, the temperature of the rolls and of the material being worked.

The speed of the front roll of a mill is largely limited by safety considerations for workmen. We have found a surface speed of about 93 feet per minute preferable for the front roll of an 84-inch mill. Higher speeds result in increased power requirements, with accompanying difficulties in temperature and plasticity control, and with no saving in the time for adding compounds.

Power input increases with an increase in friction ratio, and peak loads are higher. Since the plasticizing of rubber is fastest at ratios above one, but under 1.30, and since compounds are incorporated in a mix most efficiently at even roll speeds or at low friction ratios, it would, therefore, be theoretically advantageous to employ separate mills for these particular purposes. But the inflexibility of such an arrangement suggests a compromise. We have chosen a ratio of 1 to 1.23 for 84-inch mills used both for plasticizing rubber and for mixing stocks, and a ratio of 1 to 1.10 for 60-inch mills employed for mixing only. If a heavily compounded stock is mixed on the fast roll of a mill, the rate at which the compound is incorporated is usually faster, with a slight decrease in power consumption.

We know that power input increases with the gauge of the stock. Up to one inch the average increase in power is a little under 20% for each quarter-inch. It may be of interest to mention that we have discarded the practice of breaking down or plasticizing rubber on roll mills for a specified time in favor of a gauging method. Due to the variations in crude rubber and in mill temperatures, breaking down for a set time resulted in wide differences in plasticity. It is found that, if time is disregarded and temperature ranges are reasonable, plasticity can be more accurately controlled by milling until a sample of the rubber cut from the roll gauges a certain thickness. The method effects power as well as labor savings, since reprocessing is minimized.

We have repeatedly noted that power loads are less when rubber is worked on hot mills or in internal mixers at high temperatures than at low temperatures. But the rate of permanently softening is necessarily slower, so that the total power consumption is not reduced, but is increased.[8] However, power may be saved by practices which evade the losses incidental to getting cold rubber or stocks properly working on a mill or in an internal mixer.

Charts Show Power Consumption

From actual power charts we have plotted curves in a form that more clearly illustrates some of the effects when we break down rubber or when mixing stock. Figure 1 shows some of the effects noted in the process of breaking down rubber on a standard 84" roll mill. The final plasticity figure (Williams, K_3) was .339, with a recovery of .051, the operation requiring a total power consumption of 32.94 K. W. H., or 0.1098 K. W. H. per pound. The batch was cooled to room temperature, and was worked on the mill again to the point where it ran smooth (Fig. 2). This resulted in a further softening to a plasticity of .300, with a recovery of .032. Just before slabbing off the batch in the first operation, the plasticity of the rubber was .363 and the recovery .063; at

[8] W. W. Vogt, *Rept. of Phys. Test. Com.*, Rub. Div., A. C. S., April, 1924.

that point a total of 26.86 K. W. H., or .0895 K. W. H. per pound. had been used (Fig. 1). Warming up the cooled batch as described (Fig. 2) required an additional 20.82 K. W. H. total, or .0694 K. W. H. per pound. These comparisons indicate a considerable loss in power during the period of getting the rubber actually working and plasticizing on the mill.

Figure 3 was plotted from a characteristic chart of the power input in breaking down crude rubber in a No. 27 Banbury mixer. It will be noted that several minutes are lost while charging the rubber into the machine. A longer throat might improve the condition, but a change in this construction detail is not needed for mixing operations.

Some average power consumption figures for mixing master batches in a No. 27 Banbury are as follows:

Master Batch Approximate Components	*Sp. Gr.*	*Pounds*	*Time Mins. Total*	*K.W.H. Per Lb.*	*Plas- ticity.*	*Rec'v'y*
Rubber 55%, carbon black 40%, softener 5%.....	1.15	835	20	0.0704	.734	.082
Rubber 33%, reclaim 34%, carbon black 30%, softener 3%..	1.20	862	20	.078	.800	.22
Rubber 67%, softener 33%....	0.91	1,050	45	.101	.235	.04
Rubber 90%, softener 10%....	0.95	750	20	.097	.310	.02

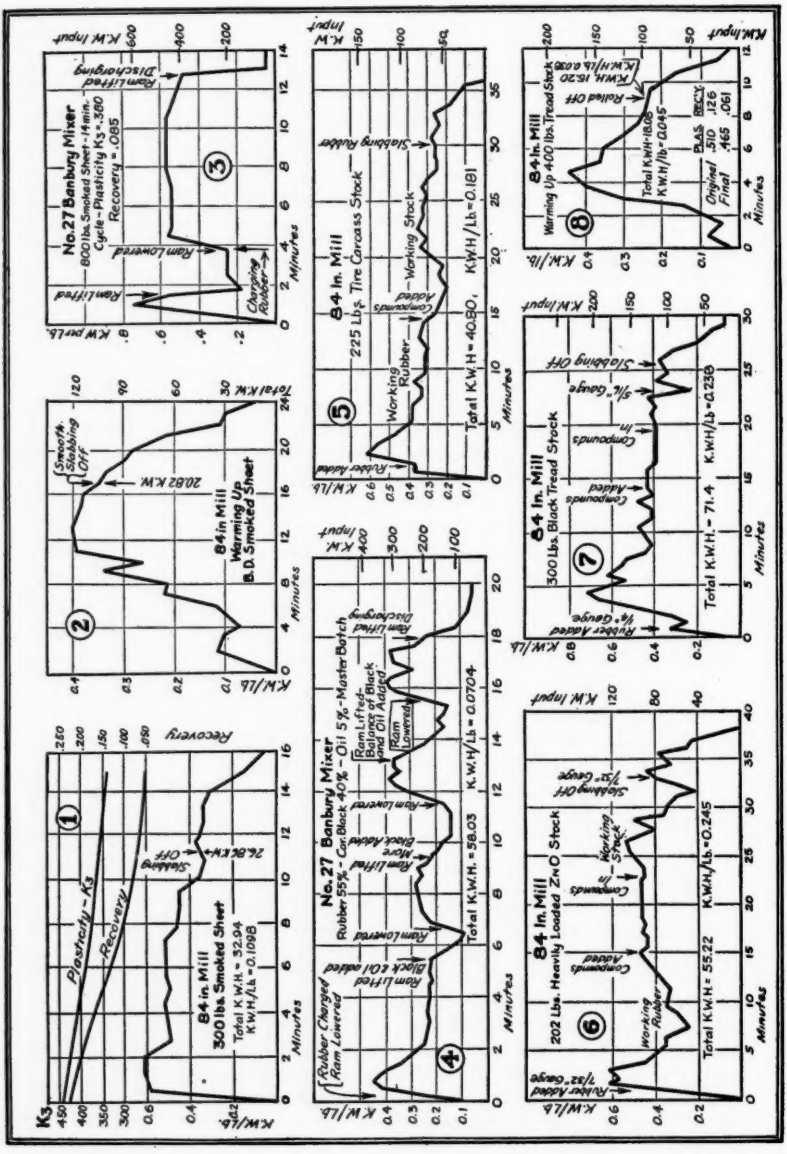
Figure 4 refers to the operation of mixing in a No. 27 Banbury mixer a master batch of approximately 55% crude rubber, 40% carbon black and 5% softener. The variations in power input with the different operations are distinctly evident. The advantages of preparing master batches on a large scale, followed by blendings and by the addition of sulphur, opens an especially extensive field for the internal mixer. It is by far the most efficient machine for mixing master batches, and introduces large savings in power, as well as in other costs. The smaller factory can employ the internal mixers with less capacities in such processes, although necessarily with somewhat lower relative profits.

Figure 5 shows the power effects in mixing a high-grade tire carcass stock. Figure 6 refers to a stock heavily loaded with zinc oxide. A representative curve for a high carbon black tread stock is shown in Figure 7, while the power used in warming up that stock for calendering or tubing is indicated in Figure 8.

Apron Mill Uses Less Power

Aside from other considerations, an improvement over the plain roll mill is the so-called apron mill, equipped with a conveying belt which continuously returns materials to the "nip" of the rolls. Compared with regular 84" mills for breaking down smoked sheet to the same degree, the 84" apron mill gives not only as much as 15% greater production, but there is about 4% less power consumption, with a 10% increase in loads. The lower power consumption may be explainable by the fact that the apron keeps the sheet of rubber closer to the mill and constantly feeds a rolling bank of material to the nip of the rolls, while during the first stage of milling the plain mill squeezes rather than works the loose sheet returning to the nip. An additional saving is realized when mixing stocks, due to a more rapid incorporation of compounds.

Herewith are shown some power comparisons for mills and internal mixers. All data on mills refer to 84" machines, with the front,



Figures 1 to 8 Showing Power Consumption in Various Milling Operations

or 26" diameter, rolls running at 93 feet per minute, and with the face speed of the back, or 22 3/16" diameter, rolls at 104.6 feet per minute. This is a ratio of 1 to 1.23. The internal mixer was a No. 27 Banbury, with rotors running 14.5 R. P. M. and 12.5 R. P. M., respectively.

We continue to conjecture about the amount of money we spend for power that is greedily gobbled up by that wanton waster, mechanical friction. C. H. Young of the Dunlop Rubber Company of England has made some observations on the power lost as friction in the four bearings of a mill and in the driving gearing. He noted that a mill running idle with rolls set apart required under 5% of the power input of that at full load. But he calculated that under load as much as 40% of the power input is lost as friction in bearings and gearing. That statement has been challenged, and there are estimates that these losses may be nearer 10%. It must not be forgotten that the housings and other parts of mills are excellent radiators of heat, and that the bearings are indirectly cooled to some extent by the water in the rolls. We have evidence which indicates that friction losses in milling machinery are over 20% of the total power input. Mr. Young proposed roller bearings as a means of reducing these losses possibly

POWER COMPARISONS FOR MILLS AND INTERNAL MIXERS

	Batch Lbs.	*Total Time Mins.*	*Avg. Load H.P.*	*Peak Load H.P.*	*K.W.H. Per Lb.*	*Plas. Average*	*Rec'y Average*
SMOKED SHEET:							
84" Mill	400	20	125	175	0.102	.370-.410	.080-.120
84" Apron Mill..	300	12-14	135	175	0.0983	.370-.410	.080-.120
No. 27 Banbury (with sheeter)	800	14	400	600	0.090	.370-.410	.080-.120
TIRE CARCASS STOCKS:							
Sp. Gr. 0.97. (Using B.D. Rubber)							
84" Mill	150	30	90	150	0.176	.315	.014
84" Apron Mill..	150	25	95	150	.164	.315	.014
No. 27 Banbury..	750	10	350	550	.068	.315	.014
(Sulfur Mills)....		....	.....	.....	.048	.....	.....
HIGH C BLACK TREAD:							
Sp. Gr. 1.12 (Using Rubber K_8=.390, Recovery=.100)							
84" Mill	300	30	87	137	0.238	.480	.065
84" Apron Mill..	300	25	90	137	.220	.480	.065
No. 27 Banbury..	825	13	350	500	.074	.480	.065
(Sulfur Mills)		....	.....	.....	.058	.....	.....

90%. Immediately there arise the objections that roller bearings might not withstand the shocks to which they would be subjected, and that their cost would be very high in any event. The more efficient roller bearing is proving practicable and profitable in the place of plain bearings for railroad car wheel journals, where strains and shocks are severe. Experiments are under way now with mills. It is not too much to expect that the mechanical engineer will soon make available a satisfactory roller bearing for mill-room machinery that will effect appreciable savings in the power costs for milling and mixing rubber.

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Experiences With Mixing Mill Roll Speeds and Speed Ratios, and Batch Sizes

Erle C. Zimmerman

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THE remarks which I am about to make concerning mixing mills apply especially to 84″ mills ,with 26″ front rolls and 22″ rear rolls. Other sizes of rolls have been experimented with, and the results have been about the same as with the 26″ and 22″. The system of cooling used was that described by H. K. Jennings at the meeting of this group on February 15,* which consists of a spray pipe and open roll and a means for cleaning the inner surface of the roll. The mill was supplied with 10 gallons of 54°F. water per minute, with 5.5 gallons to the front roll and 4.5 gallons to the rear roll.

The speed and ratio of mixing mills can be most clearly described in terms of roll surface speed and roll surface speed ratio. A great variety of surface speeds and surface speed ratios are in use at the present time. Front roll surface speeds as low as 75 feet per minute and as high as 135 feet per minute can be found, and ratios run anywhere from even speed up to front roll to rear roll ratio of 1:2.

The effect of mill speeds and ratios on the mixing of stocks can be best determined by making a study of the temperature of the stock on the mill, the plasticity of the stock and the degree of uniformity of the mixing. Such information may be obtained on one mill equipped to give different speeds and ratios, or on several different mills of the same type. Whatever stock is to be experimented with should be mixed on the mill or mills in question for a few hours, after which several batches should be mixed, on which the average results are to be based. The same mill operators should be used, and the raw material should, of course, be standardized.

Six Batch Test on Two Mills

The results which I am about to describe (shown in Table 1) are the average results of six batches mixed on two mills, each

*Jennings' complete paper was published in THE RUBBER AGE, February 25, 1928 (vol. 22, pp. 532-3).

TABLE I—EFFECT OF SURFACE SPEEDS AND RATIOS

Surface Speed of Front Roll Ft./Min.	Ratio of Front to Rear Roll	Water Temperature °F.			Roll Temperature °F.		Stock Temp. °F.	Plasticity	Index of Variation In Gravity
		Supply	Front Roll Exhaust	Rear Roll Exhaust	Front	Rear			
90	1:1.07	54	88	88	131	130	195	3.65	.060
98	1:1.07	54	89	89	133	132	205	3.62	.044
113	1:1.07	54	91	87	137	134	216	3.70	.031
76	1:1.27	54	85	86	116	124	188	3.61	.083
83	1:1.27	54	86	86	120	128	194	3.67	.063
96	1:1.27	54	88	89	126	133	207	3.70	.042
76	1:1.07	54	82	83	116	119	176	3.65	.091
76	1:1.27	54	85	86	116	124	188	3.61	.083
76	1:1.64	54	86	90	120	135	199	3.75	.096

of three different speeds and ratios. The stock was a high quality cord tire tread, and was mixed at the rate of 275 pounds in 33 minutes. At the end of the mixing period test samples were cut from both ends and the center of the mill simultaneously. The roll temperatures were measured by a Cambridge surface pyrometer. The stock temperatures were measured by means of a potentiometer indicator and a thermocouple, the junction of which was folded in the stock while it was being cut from the mill. Plasticity determinations were made on the three test samples by the Williams method, the "Y" value for 5 minutes at 85°C being recorded. The index of variation in specific gravity was obtained for each batch mixed by dividing the difference between the correct specific gravity of the stock, minus the specific gravity of rubber, into the maximum variation found in the three samples.

Comparisons to Show Effect of Speed

83 and 96 feet per minute were compared for additional data on speed. The effect of ratio was studied on a third set of three mills which had a front roll surface speed of 76 feet per minute and ratios of 1:1.07, 1:1.27 and 1:1.64. The following results were obtained: mills with a ratio of 1:1.27 and front roll surface speeds of 76,

Three mills with a ratio of front to rear roll surface speed of 1:1.07 and front roll surface speeds of 90, 98 and 113 feet per minute were compared to show the effect of speed. Similarly, three are the average results of six batches mixed on two mills, each

The results which I am about to describe (shown in Table 1)

(1) The exhaust cooling water temperature varied from 85-91°F, and showed practically the same temperature rise in all cases, being slightly higher for the faster mills.

(2) The roll temperatures varied from 130-137°F for 1:1.07 ratio mills, and were equal for both rolls. For the higher ratio mills the temperatures varied from 116-135°F, and the rear rolls ran higher than the front rolls.

(3) The stock temperatures ran 195°F, 205°F and 216°F for the 1:1.07 ratio mills, and 188°F, 194°F and 207°F for the 1:1.27 ratio mills. For both ratios the temperature of the stock increased with increased mill speed. In the case of the mills with 1:1.07, 1:1.27 and 1:1.64 ratios, the stock temperatures were 176°F, 183°F and 199°F, respectively, increasing with increased ratio.

(4) The plasticities of the stock were practically equal for mills of all speeds and ratios tested. This indicates that there is a

TABLE II—THE EFFECT OF MILL SPEED ON STOCK TEMPERATURE

Roll Surface Speeds Ft./Min.	*Surface Speed Ratios*	*Average Stock Temperature °F.*
90:97	1:1.07	200
113:121	1:1.07	213
124:134	1:1.07	221
131:142	1:1.07	234

tendency for the plasticity of the stock to be equalized, due to the relationship between mill speed and stock temperature.

(5) In regard to the uniformity of the stock, based on specific gravity, the fastest mills gave much better uniformity than the slowest mills. Low ratio mills gave just as good uniformity as the high ratio mills.

Similar experiments have been made on a single mill equipped with a variable speed motor. The data listed in Table 2 were obtained on such a mill in mixing a stock containing a high percentage of zinc oxide. Front roll speeds of 90, 113, 124 and 131 feet per minute, and a ratio of 1:1.07 gave stock temperatures of 200°F, 213°F, 221°F and 234°F.

It has been pointed out that front roll speed has a pronounced effect on the uniformity of the stock mixed. A saving in mixing time can therefore be made by increasing the speed of the mill. It has been found that tread stock which is mixed in 34 minutes on a mill with 90 feet front roll speed and 1:1.07 ratio can be mixed equally as well in 30 minutes on a mill with 113 feet front roll speed and the same ratio. The speed of the mill cannot be increased to such an extent, however, that excessive stock temperatures result, or the stock will cure up on the mill. It is not to be taken from this statement that slow mills are necessary for fast curing stocks. Fairly fast mills can be used for such stocks if the batch size is not too large. The most important fact in connection with mixing mill speeds and ratios is that a high front roll surface speed will give the most thorough mixing at the fastest rate, and that a low surface speed ratio will give a lower stock temperature than a high ratio.

The effects of batch size and mixing time are clearly shown in Table 3. Two hundred pound batches of a cord tire tread stock were mixed for 33 and 66 minutes, and compared with 300-pound batches mixed in the same lengths of time. Outside of the anticipated differences in the plasticities of the stock, no other appreciable differences could be detected. Stress at 400% elongation and tensile were determined on composite samples, representing the different mixes and the results over a range of five cures were averaged together. The stress at 400% elongation varied from 1,635 to 1,730 pounds per square inch, and the tensile varied from 3,820 to 3,910 pounds per square inch, which is no greater variation than is usually found in consecutive batches mixed according to the same specification. Similar results have been obtained in the case of various other stocks; however, there are exceptions.

In reference to the large batch versus the small batch, there is, of course, plenty to be said both pro and con. If you are considering pounds of stock mixed per minute to a given degree of uniformity, the large batch is the more desirable. If you are considering uniform plasticity, you will probably want a smaller batch.

TABLE III—THE EFFECT OF BATCH SIZE AND MIXING TIME ON THE PHYSICAL PROPERTIES OF THE STOCK

Batch Size in Pounds	*Mixing Time in Minutes*	*Plasticity*	*Stress at 400% Elongation Lbs./Sq. In.*	*Tensile at Break Lbs./Sq. In.*
200	33	4.12	1675	3890
200	66	3.95	1635	3910
300	33	4.55	1700	3820
300	66	4.25	1730	3820

If the stock is delivered direct from the mixing mill to the tube machine or calender, you will probably want a smaller batch than if your stock is stored and later warmed up. If the stock is fast curing, you will want a smaller batch. If the pigment is added in the form of a rubber master batch, you will probably find that you can mix almost the same number of pounds per minute, whether the batch is large or small. The batch size of any particular stock, therefore, depends not only on the stock itself, but on the subsequent processing of the stock.